

MOLECULAR BEAM EPITAXIAL GROWTH OF
HOMOEPITAXIAL ZINC SELENIDE

By
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The focus of this dissertation concerns the subject of ZnSe homoepitaxy. Of primary concern in the study was ZnSe wafer quality and extensive analysis was performed on wafers purchased from the Sumitomo Company of Japan that were to be employed as substrates.

The analysis of substrate material, which involved, high-resolution x-ray diffraction (HRXRD) photoluminescence (PL), transmission electron microscopy (TEM), atomic force microscopy (AFM) and etch-pit density (EPD) measurements, revealed the best ZnSe wafers supplied by Sumitomo to be suitable for a serious homoepitaxy study.

For instance, x-ray ω rocking curve linewidths (using 7-crystal optic suystem) were on the order of 8 arcsec. and defect densities were estimated in the 10^5 cm^{-2} range. In addition, a surface roughness on the order of 0.16 nm was assessed which is comparable to the surface roughness of commercial GaAs wafers.

Prior to conducting the detailed homoepitaxy study, *ex-situ* and *in-situ* ZnSe wafer treatment processes were optimized. An *ex-situ* treatment process involving a six minute UV-ozone exposure was found to be optimum with regard to surface morphology and resultant epilayer crystallographic quality. And, in terms of *in-situ* processing, a combined hydrogen atom/thermal treatment was found to result in the elimination of surface oxides at temperatures as low as 300 °C (compared with 500 °C for conventional thermal treatment).

ZnSe homoepitaxial layers were grown on suitably prepared substrates by conventional molecular beam epiatxy (MBE) and using a novel growth mode which we term “Surface Relaxation Controlled Epiatxy” (SRCE). In both cases, following *in-situ* wafer cleaning, the ZnSe substrates were exposed to a Se flux for about two minutes during which time a Se-stabilized surface developed as evidenced by the development of a (2x1) surface reconstruction.

Thereafter, in the case of SRCE, the substrate was alternately exposed to Zn and Se, in each case the “shutter open” or exposure time was the same, namely 30 seconds. The delay time, however, the time allowed to elapse between closing the Zn shutter and opening the Se shutter, or vice-versa, was systematically varied from run-to-run over the range, 0 to 60 seconds.

In all cases, this growth mode was in effect for 10 cycles (10 Zn exposures and 10 Se exposures) beyond which conventional MBE growth was performed (both Zn and Se shutters permanently open) until 2 μm of ZnSe had been deposited.

ZnSe homoepitaxial layers grown using the SRCE growth mode at the initial stages of the growth were characterized by a number of techniques including low-temperature PL, HRXRD, TEM and etch-pit density measurements and it was found that the delay time strongly affected the defect density in the films. An optimum delay time was found for the Se surface which resulted in the lowest defect density films and a model is presented to explain this phenomenon.

CHAPTER 1 INTRODUCTION

Motivation and Objectives

Zinc selenide and related II-VI compound semiconductors have for several years been the subject of intense research because of their potential for use in the fabrication of optoelectronic devices operating in the blue-green region of the electromagnetic spectrum, specifically, blue-green light emitting diodes (LEDs) and laser diodes (LDs). Traditionally, epitaxial growth of ZnSe and related II-VI compound semiconductors has been conducted on GaAs substrates because of the small lattice mismatch between ZnSe and GaAs (0.27 % at room temperature) and because of the commercial availability of very high quality, reasonably priced GaAs wafers. In addition, surface preparation procedures for subsequent epitaxial growth on GaAs substrates are well established. However, despite these advantages, there are some drawbacks associated with using GaAs as a substrate material for wide-gap II-VI based injection devices.

Firstly, epitaxial ZnSe on GaAs experiences significant biaxial strain which can cause the formation of misfit dislocations in the epilayer. The biaxial strain is a consequence of the small but significant lattice mismatch of this system, and the different thermal expansion coefficients exhibited by these two materials [1]. The lattice mismatch problem can be overcome by depositing ternary or quaternary alloys such as ZnSSe or

ZnMgSSe on GaAs; for instance, $\text{ZnS}_x\text{Se}_{1-x}$ ($x \approx 0.06$) is lattice matched to GaAs at typical growth temperatures (250 ~ 300 °C). However, tensile strain and hence, misfit dislocations, develop in these materials systems at the heterointerface as the sample cools from the epilayer growth temperature to room temperature due to the difference in thermal expansion coefficients of the epilayer and the substrate [2, 3].

Secondly, the presence of an interfacial compound at the ZnSe/GaAs interface has been identified by several authors [4-6]. Tu and Kahn [4] reported that the ZnSe/GaAs interface is nonstoichiometric and includes a thin intermediate (Ga, Se) compound layer due to a Se-As exchange taking place during the early stages of growth. Later, Li et al. [5] suggested that this thin intermediate (Ga, Se) compound layer could be a vacancy-rich Ga_2Se_3 compound based on their TEM results. Wright and Williams [6] also detected the presence of this compound at the ZnSe/GaAs heterointerface using high-resolution TEM. These authors observed that the Ga_2Se_3 layer was approximately 2 nm thick and corresponded to the width of 3~4 unit cells of Ga_2Se_3 . This compound layer could act as a source of defects at the heterointerface since the Ga_2Se_3 layer is a vacancy rich, highly defective structure.

Finally, an electron transport barrier exists at the n-GaAs/n-ZnSe (or other ZnSe-based material) heterojunction. Until recently, this problem had not been considered a severe obstacle to device development probably because it was overshadowed by a much more severe problem: the inability to make ohmic contact to p-type ZnSe. However, now that various schemes have been developed for making ohmic contact to p-ZnSe, the electron transport barrier at the n-GaAs/n-ZnSe interface seems to have grown in relative

importance. In present-day diode laser structures, electron injection occurs from n-GaAs into the n-ZnSe-based material. A finite conduction band potential energy discontinuity is present having a magnitude in the range, $\Delta E = 100\text{-}300$, meV for GaAs/ZnSe (and even larger for GaAs/ZnMgSSe), contributing to a finite heterojunction impedance [7].

The three problems discussed above are a direct result of the heterointerface between ZnSe (or related compounds) and GaAs. A more ideal approach, at least in principle, would be to use ZnSe wafers as substrates. However, until recently, the non-availability commercially of good quality ZnSe wafers severely hampered efforts to develop ZnSe homoepitaxy.

Recent efforts by the Sumitomo Electric Company of Japan, however, have resulted in the production and commercial supply of ZnSe wafers of sufficient crystallographic quality to permit a serious study of ZnSe homoepitaxial growth.

The present work in the ZnSe homoepitaxy area had several objectives which were as follows: First, to characterize the Sumitomo ZnSe wafers in terms of purity, crystallographic quality and surface quality. Second, to develop suitable *ex-situ* and *in-situ* wafer preparation procedures for epitaxy. Third, to investigate homoepitaxial layer quality by growing on suitably prepared surface. And fourth, to investigate the stacking fault issue as it pertains to homoepitaxy.

Prior to outlining the scope of the present work, a literature review section follows.

Literature Review

Blue-Green Laser Diode Development History

Since p-type doping of ZnSe using a rf plasma discharge, nitrogen free-radical source was successfully achieved by Park et al. [8], research on the wide-gap II-VI compound semiconductors has been dramatically revitalized in an effort to realize the fabrication of blue-green light emitting diodes (LEDs) and laser diodes (LDs). As a result, Haase et al. [9] in 1991 were able to demonstrate the operation of the first ZnSe-based blue-green laser diode by employing the new p-type doping technique and incorporating a $\text{Cd}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSe}$ single quantum well active region. Such devices were operated in the pulsed-mode at 77K and the lasing wavelength varied over the range, 490 to 520 nm, depending on the concentration of Cd in the quantum well material.

However, this blue-green laser diode had two major drawbacks associated with its structure. Firstly, a small but significant lattice-mismatch existed at the cladding/guiding layer interfaces (interfaces between the ZnSSe and the ZnSe layers in the vicinity of the active region). The lattice-mismatch resulted in the presence of dislocations in as-grown structures which in turn led to rapid device failure. Secondly, the gold contact to the p-ZnSe on top of the device was highly rectifying in nature which meant that a significant portion of the voltage applied across the device was dropped across the Au/p-type contact.

In order to eliminate the formation of misfit dislocations due to lattice mismatch, a quaternary alloy, $\text{Zn}_{1-x}\text{Mg}_x\text{S}_y\text{Se}_{1-y}$, was developed as the cladding layer of a laser diode by Okuyama et al. [10]. With values of $x=0.87$ and $y=0.18$, $\text{Zn}_{1-x}\text{Mg}_x\text{S}_y\text{Se}_{1-y}$ could be

lattice-matched to GaAs and to a particular composition of $\text{ZnS}_y\text{Se}_{1-y}$. Consequently, a completely lattice-matched diode laser structure could be envisioned which would include lattice-matched cladding/guiding layer interfaces. Also, since the quaternary material was reported to have a significantly smaller refractive index than that of ZnSe, enhanced optical confinement could be achieved using the alloy as cladding layer material. This new quaternary material led to the development of continuous wave operation of ZnSe/ZnMgSSe laser diodes at 77K by Okuyama et al. [11] in 1992. They reported blue stimulated emission at a wavelength of 447 nm and the threshold current density was 225 A/cm^2 . In May 1993, Gaines et al. [12] introduced the first pseudomorphic separate confinement heterostructure (SCH) laser diode containing $\text{Zn}_{1-x}\text{Mg}_x\text{S}_y\text{Se}_{1-y}$ cladding and $\text{ZnS}_{0.06}\text{Se}_{0.94}$ guiding layers. They reported that lasing was observed at temperatures as high as 394K in the pulsed mode (threshold current density was 500 A/cm^2 at room temperature). Continuous-wave operation of blue-green laser diodes at room temperature was also reported by Nakayama et al. in August, 1993 [13]. In this case, stimulated emission was observed at a wavelength of 523.5 nm with a threshold current of 45 mA (1.4 kA/cm^2) from ZnCdSe/ZnSe/ZnMgSSe, single-quantum well (SQW) SCH laser diodes. However, ohmic contact to the p-ZnSe had not been achieved at that time; contact to the p-type ZnSe was made using Au/Pd or Au, both of which form Schottky barriers.

While ohmic contact to n-ZnSe and other n-type II-VI materials is easily made, the same is not true for p-type ZnSe and its related alloys as a consequence of the deep

valence band of ZnSe. Four p-type contact schemes, however, have recently been developed:

Highly doped p-ZnSe In this method, a heavily doped p-ZnSe:N contact layer is grown at a low growth temperature of 150 °C using thermally cracked Se; Au was used for metallization [14].

Mercury Selenide An epitaxial layer of p-HgSe is deposited by MBE on p-ZnSe [15]. HgSe has a work function of about 5.9 eV which is approximately 0.5 eV less than that of the most heavily doped p-ZnSe currently possible (6.4 eV).

Pseudo-graded structure A pseudo-graded p-ZnTe/ZnSe heterostructure was grown by MBE on p-ZnSe [16]. ZnTe has a band gap energy of 2.3 eV; heavy p-type doping of ZnTe can be easily achieved by using the nitrogen plasma source [17]. Theoretically, by sandwiching a graded layer of p-ZnTe_ySe_{1-y} between p-ZnSe and p-ZnTe, where y varies from 0 to 1, ohmic contact to p-ZnSe can be achieved. However, the ternary ZnTe_ySe_{1-y} is difficult to grow because the Te content cannot be faithfully reproduced. A pseudo-graded structure of p-Zn(Se,Te) was used.

Multiple quantum well structure The growth of a ZnSe/ZnTe multiple quantum well hole resonant tunneling structure between layers of p-ZnSe and p⁺-ZnTe are grown on p-ZnSe [18].

The ohmic contact schemes described above have been successfully incorporated into blue-green diode laser structures and have resulted in dramatically lower operating voltages (around 6V versus 15V for earlier devices) as reported by Nakayama et al. [13]

using the multiple quantum well contact scheme and by Salokatve et al. [19] using the pseudo graded contact structure. Since then, several research groups reported success in achieving laser action at room temperature in closely related structures. [20-28]. Despite these successes, however, a problem remains with wide-gap II-VI/GaAs laser diodes in that the devices fail rather quickly, the best devices failing in the one-to-two hour time frame.

Wide-Gap II-VI/GaAs Laser Diode Failure Mechanisms

Since the first demonstration of a blue-green injection laser at 77K in 1991 [9], enormous progress has been made in the areas of material development, electrical contacts, and design/processing techniques to realize continuous-wave operation of blue-green diode lasers at room temperature. However, of major concern at the present time regarding the performance of ZnSe-based blue-green diode lasers grown on GaAs substrates, is their short operating lifetimes. The “best” devices reported by the 3M and Sony Corporations, for instance, have lifetimes currently between one and two hours operating in the continuous-wave mode at room temperature. Consequently, the identification of device degradation mechanisms has become a major focus of attention [29-39]. In this section degradation mechanisms for blue-green laser diodes and light emitting diodes reported so far will be reviewed to provide an understanding of the role of defects in device failure and to gain insight into methods of minimizing those defects or completely eliminating them.

Laser diodes fail primarily due to a reduction of gain in the active region which is evidenced by the growth of $\langle 100 \rangle$ dark line defects (DLDs) [30, 34, 36]. During device operation, pre-existing defects such as paired V-shaped stacking faults and threading dislocations associated with them can act as high-diffusivity channels for point defects which are known to be present in II-VI materials grown by MBE on GaAs substrates. It is believed that these point defects act as non-radiative recombination centers and are clustered in the vicinity of the pre-existing defects and explain the gradual darkening of the dark spot defects [36]. These point defects can be transported to the quantum well-active region by so-called pipe diffusion along threading dislocations. Once point defects or point defect complexes reach the quantum well-active region by virtue of transport along the threading dislocations, they spread out within the quantum well by non-radiative recombination-enhanced motion under external injection of electrons and holes. It is believed that a multiphonon recombination process provides enough energy to the lattice to cause defect reactions by recombination-induced defect heating [38] which enhances the migration of the point defects.

According to Guha et al. [36], the enhancement of the diffusion rates of point defects due to such non-radiative recombination during normal device operation is appreciable and can explain the propagation of the degradation defects. It is believed that the most probable explanation for $\langle 100 \rangle$ dark line defects (DLDs) is point defects and/or point defect clusters [36, 37, 40]. It is unclear, however, why the point defects would preferentially align themselves along the $\langle 100 \rangle$ directions. The point defects can aggregate locally in the vicinity of misfit dislocations at the interfaces between quantum

well-active region and guiding layers as a consequence of interaction with the defect stress fields, and result in the nucleation of small dislocation loops that can propagate to form the dislocation network. Consequently, major attention currently is focused on the pre-existing V-shaped stacking faults which are growth defects formed at the II-VI/GaAs heterointerface and which propagate upwards with growth forming a V shape. They can not only act as misfit dislocation sources once a strained quantum well is introduced, but they can also act as non-radiative recombination sources [31]. Unfortunately, the specific origin of stacking faults is not identified.

As discussed in the previous section, since the Ga_2Se_3 compound layer that forms at the interface between ZnSe and GaAs is a vacancy rich, highly defective structure, a strong possibility exists that this layer may be the source of stacking faults at the II-VI/GaAs heterointerface.

Homoepitaxial ZnSe

Since Park et al. [41] reported for the first time the homoepitaxial growth of ZnSe by molecular beam epitaxy, there have been few reports in the literature concerning this topic. The paucity of research in this area is due primarily to the difficulties associated with growing bulk ZnSe crystals and the nonavailability commercially of high quality, high purity, large area wafers

The early stage of homoepitaxial ZnSe research was hampered by the poor quality of the ZnSe substrate material and was mainly concentrated on substrate surface preparation and removal of the oxide layer. The first MBE growth of homoepitaxial

ZnSe was reported by Park et al. [41] in 1985. In their work, centimeter-size (100) ZnSe wafers obtained from Eagle-Picher Industries, Inc. were used as substrate materials. The low temperature photoluminescence spectra recorded from the ZnSe substrates were dominated by donor-acceptor (DA) pair recombination peaks, indicating the presence of extrinsic impurities. Accordingly, the quality of the MBE grown homoepitaxial ZnSe was limited by the poor quality of the substrate wafer. In 1988, Menda et al. [42] reported homoepitaxial ZnSe growth by MBE. These authors used an etching solution of ($\text{H}_2\text{O}_2 + \text{NH}_4\text{OH} + \text{H}_2\text{O}$) to remove the polishing damage from the wafer surface. In this case, the ZnSe epilayer quality was also limited by the poor substrate quality. At the same time, Ohishi et al. [43] grew homoepitaxial ZnSe layers on ZnSe substrates with (110) and (111) surface orientations. The substrate surfaces were prepared by chemical etching using a chromic acid mixture or a mixture of ammonia and hydrogen peroxide solution. PL spectra recorded at 4K from the epitaxial layers showed strong Y and S emissions (defect related emissions) and a broad band in the low energy regime. In 1990, Park et al. [44] reported the growth of high purity homoepitaxial ZnSe grown on substrates produced in-house at the Nippon Sheet Glass Co. in Japan, however, this substrate material was never made commercially available. Park et al. employed a Br_2 -methanol etch to remove polishing damage.

A dry-etching method using BCl_3 gas was employed to remove the polishing damage at the ZnSe substrate surface by Ohkawa et al. [45-47]. These authors reported that they could remove the surface damage created by polishing and slicing during wafer production using a BCl_3 gas plasma and could obtain mirror-like surface morphology

after etching about 10 μm . Again, however, low temperature PL analysis revealed that the ZnSe homoepitaxial layers also suffered from poor substrate quality (dominant Γ_1^d emission and deep level emission at around 2.4 eV).

Recently, a bulk crystal growth technique known as seeded physical vapor phase transport (SPVT) was employed to grow large-area high-quality ZnSe crystals by the Eagle-Picher Company [1], [48]. By using these SPVT-grown ZnSe wafers, Ren et al. [49] reported the MBE growth of ZnSe-based light emitting diodes (LEDs) and photopumped lasers. Ren et al. employed conventional thermal cleaning to remove the surface oxide which resulted in an elongated spot (not streaky) RHEED pattern having a (3x1) surface reconstruction obtained by holding the substrate temperature at about 480 $^{\circ}\text{C}$ for 5 minutes. At the growth temperature (250 $^{\circ}\text{C}$), ZnSe nucleation was initiated by simultaneously opening both Zn and Se source shutters (Zn:Se beam pressure ratio of 1:2). It was found that the RHEED pattern changed immediately from an elongated (3x1) to a streaky (2x1) reconstructed pattern. Based on their TEM results, these authors claim that they did not observe any dislocations either at the homointerfaces or in the epilayers; they estimated the dislocation density to be about 10^5 cm^{-2} . However, more detailed information to assess the structural quality of their homoepitaxial layers was not provided.

Shortly thereafter, Eason et al. [50] reported the fabrication of high-brightness blue and green LEDs based on II-VI heterostructures grown by MBE on Eagle-Picher ZnSe substrates. A $\sim 0.1 \mu\text{m}$ thick $\text{Zn}_{0.9}\text{Cd}_{0.1}\text{Se}$ active region was used for the blue LEDs, whereas a $\text{ZnSe}_{0.9}\text{Te}_{0.1}$ active region was employed to produce green LEDs. The

electroluminescence from the ZnCdSe blue LED which peaked at 489 nm had a full width at half maximum (FWHM) of 72 meV. They also reported that the dislocation density in the devices grown on ZnSe was about 10^6 cm^{-2} based on preliminary x-ray diffraction and TEM results; however, none of those data were provided.

Around the same time, we reported the results of a preliminary study concerning the MBE growth of green LEDs on ZnSe wafers which were purchased from the Sumitomo Electric Industries, Co [51]. Conventional thermal treatment as well as H-atom treatment methods were compared for ZnSe wafer cleaning. In the case of thermal cleaning, evidence of oxide desorption was only apparent at temperatures approaching 500°C and at these temperatures surface roughening became apparent as evidenced by the observation of a spotty RHEED pattern. Conversely, we found that clean, atomically smooth surfaces could be obtained at much lower temperatures ($<380^\circ\text{C}$), as evidenced by the observation of a streaky RHEED pattern, in the case of a combined thermal/H-atom treatment process, a hydrogen plasma being remotely generated from a rf plasma discharge source (see Chapter 4). Hall-effect measurements were also performed on nitrogen-doped p-type ZnSe/S.I. ZnSe epilayers which revealed free-hole concentrations in the homoepitaxial material as high as $2.1 \times 10^{17} \text{ cm}^{-3}$ with room temperature and 77K hole mobility values of 20 and $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively [51]. In addition, we reported the fabrication of green LEDs grown on the Sumitomo ZnSe wafers having $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{Se}/\text{ZnSe}$ multiple quantum well (MQW) active regions which exhibited an electroluminescence peak at 508 nm with a FWHM value of 47.5 meV (9.9 nm).

In summary, the early stages of MBE growth of homoepitaxial ZnSe were mainly concerned with *ex-vacuo* and *in-situ* surface preparation procedures and homoepitaxial layer quality was strongly affected by both surface preparation and the ZnSe substrate quality. However, recent reports have suggested significant promise for ZnSe homoepitaxy when good quality ZnSe wafers are employed.

Migration Enhanced Epitaxy

Introduction

Migration enhanced epitaxy (MEE) was developed as a method of enhancing the surface migration of adatoms on the growth surface [52, 53]. MEE growth is a modification of the MBE growth technique and is similar to atomic layer epitaxy (ALE) but without the requirement of growing exactly one monolayer per deposition period. In MEE, one cycle consists of exposure of only one of the elements forming a binary compound followed by exposure of only the other element. The period of no deposition is inserted by some researchers to insure that a shutter is completely closed before the next shutter is opened, thereby avoiding any simultaneous deposition of Zn and Se [53, 54] in the case of ZnSe, for instance. In this section, the basic principles of MEE growth will be reviewed. In addition, some examples of MEE growth will be introduced.

Basic principles of MEE growth

Originally, MEE was developed to achieve low-temperature growth of high-quality GaAs and AlGaAs epilayers [52, 53, 55, 56]. The low-temperature growth of

GaAs and AlAs is highly desirable for obtaining very sharp doping profiles for both n- and p-type dopants. It is also useful for the growth of abrupt junctions such as those required for superlattice structures. In conventional MBE growth of GaAs and AlAs, the Ga and As atoms on an As-stabilized surface migrate very slowly especially at low temperatures [52]. Indeed, it was found that the activation energy of Ga surface diffusion during GaAs growth on an As-stabilized (2x4) surface is quite large ($E_D = 1.3$ eV) [57]. For the diffusion of Al, an E_D of 1.6 eV was estimated by the same authors [57]. It is believed that these large activation energies may make the surface adatoms almost immobile when the growth temperature is low (200°C~300°C). However, fast Ga atom migration during MBE growth of GaAs has been observed by Nagata and Tanaka [58]. These authors used a shadowing method to determine Ga surface diffusion distances in the growth of (001) oriented GaAs films under both Ga- and As-stabilized conditions. In their shadowing method, geometrically obstructed microstructures were formed on (100) GaAs substrate surface by etching and using a standard photolithographic technique. In addition, the Ga and As sources were situated in two orthogonal directions of [110] and $\bar{[110]}$, respectively, and were directed at an angle of 25° from the normal to the GaAs surface. These obstructed microstructures and inclined sources provide proper conditions for selective epitaxy and make self-masking (shadowing) epitaxy. For a growth temperature of 550°C these authors found Ga diffusion lengths of ≤ 200 Å under As-stabilized condition, but the diffusion length for the Ga-stabilized growth was 1900 Å.

This large difference for the Ga diffusion length under As- and Ga-stabilized conditions was explained as follows [52]. In conventional MBE growth, the growth of

GaAs and AlAs layers is performed under As-stabilized condition. In this situation, migrating entities on the growing surface may be Ga-As and Al-As molecules or GaAs islands rather than isolated Ga and Al atoms because impinging metal atoms immediately react with arsenic molecules to form Ga-As and Al-As molecules. These molecules migrate very slowly as evidenced by high migration activation energies [57, 58]. When Ga or Al atoms impinge in an arsenic free atmosphere, they migrate on the growing surface in atomic form. Thus, surface migration is effectively enhanced at low temperatures utilizing the Ga-stabilized condition.

MEE growth of ZnSe on GaAs

Growth of ZnSe on GaAs(100) substrates by conventional MBE and migration-enhanced epitaxy (MEE) was examined by Lilja et al. [59]. In their study, they examined whether or not the exposure duration of the surface to Zn or Se flux had any influence on MEE growth by changing the Zn and Se shutter open durations. In this case, no time interval or delay time was introduced between shutter open and closed events. They found that the growth per cycle remained constant regardless of the shutter open duration and the Zn/Se BEP ratios within a certain range of growth parameters (one cycle being (1)simultaneously opening the Zn shutter and closing the Se shutter, (2) simultaneously closing the Zn shutter and opening the Se shutter). These authors concluded that ZnSe MEE growth is self-regulatory and that the total film thickness is solely determined by the number of cycles performed. This self-limiting growth characteristic of Zinc chalcogenides was also observed by other authors [60, 61]. When alternating between the

Zn and Se_n beams, MEE growth proceeded via sequential alternation of c(2x2) and (2x1) reconstructions. Based on their x-ray rocking curve measurements, Lilja et al. concluded that MEE-grown films had higher structural perfection than MBE-grown films.

High quality ZnSe/GaAs superlattices were grown by MEE [62]. To grow the ZnSe layer, beam flux durations for the Zn and Se beams were 10 s each and it was observed that the RHEED pattern changed from c(2x2) on completion of the Zn supply to (2x1) on completion of the Se supply, as the Zn and Se beams were alternated. Flat and abrupt interfaces between ZnSe and GaAs were observed by TEM.

Gaines et al. [54] examined the structural properties of ZnSe films grown by MEE. During growth, deposition times (i.e., shutter open times) for Zn and Se were about 2.5 s, and time delays of 0.2-0.3 s were added between depositions to insure that one shutter closed completely before the next opened. These authors found that the heterointerface played a significant role in determining the structural properties of the ZnSe films. For instance, the structural quality of the MEE-grown films of ZnSe was highest when the substrate was first exposed to a Zn flux for 30 s. In this case, the critical thickness for dislocation formation was approximately doubled (~3000 Å). MEE growth that began with an exposure of the GaAs substrate to a Se flux resulted in slightly higher defect densities. Therefore, it was concluded that even though the structural quality of MEE grown films (both Zn-initiated and Se-initiated) was higher than that of MBE-grown films, the quality of the MEE grown films was strongly dependent upon how the MEE growth was initiated on the GaAs substrate.

Scope of The Dissertation

This dissertation consists of six chapters. Chapter 1 states the motivation and objectives for this work and reviews the background pertaining to the subject matter. Chapter 2 describes the MBE growth system and characterization techniques used in the study. Since atomic force microscopy (AFM) and high-resolution x-ray diffraction are relatively new techniques, the basic principles of these techniques have been reviewed. Chapter 3 details the characterization results for Sumitomo ZnSe wafers. In Chapter 4, the effect of UV-ozone treatment on ZnSe wafer surface roughness is discussed and the optimum UV-ozone exposure time is identified. The influence of surface roughness on the quality of homoepitaxial epilayers is also described. Chapter 5 introduces the subject of a novel growth mode which we term, Surface Relaxation Controlled Epitaxy (SRCE) and the influence of SRCE on the stacking fault density in ZnSe homoepitaxial films is discussed.

In Chapter 6, a summary of the important conclusions drawn from this study is presented along with suggestions for future research in this area.

CHAPTER 2

MBE GROWTH SYSTEM AND CHARACTERIZATION TECHNIQUES

Introduction

All homoepitaxial ZnSe samples were grown using the molecular beam epitaxy (MBE) technique and were characterized using various analytical techniques including atomic force microscopy (AFM), photoluminescence (PL), high-resolution x-ray diffraction (HRXRD), transmission electron microscopy (TEM), and etch-pit density (EPD) measurements. All MBE growths and characterization works were carried out by the author with the exception of PL analysis which was performed by Dr. Ludwig in Dr. Hummel's laboratory at University of Florida, and selected samples were sent to the 3M Company for etch-pit density (EPD) measurements. The MBE growth conditions employed and the characterization techniques mentioned above are outlined in this chapter.

MBE System and Sample Growth

A custom-designed MBE system was used to grow all homoepitaxial ZnSe samples. The MBE system, as illustrated in Figure 2.1, consists of an ultra-high vacuum growth chamber equipped with conventional thermal effusion sources for Zn and Se, a RHEED system for assessing surface oxide removal and for observing surface atomic

structure during growth and a rf plasma discharge source to produce atomic hydrogen. Each of these sources is equipped with a movable shutter for beam control.

The ZnSe substrates were obtained from Sumitomo Electric Industries, Ltd. and had (001) $\pm 0.5^\circ$ surface orientation. The characterization results for the Sumitomo ZnSe wafers will be detailed in Chapter 3. Prior to growth, the substrates were treated in a UV-ozone system and the UV-ozone treatment will be explained in detail in Chapter 4. After being exposed to UV-ozone, the substrates were attached to a Mo holder using molten, high-purity In and the Mo holder was then immediately loaded into the growth chamber of the MBE system via an entry/exit chamber. The growth conditions for all samples were the same in order to exclude any influence due to the growth condition variation on epilayer quality and the growth conditions employed during conventional MBE are summarized in Table 2.1.

Table 2.1 Typical growth conditions for homoepitaxial ZnSe growth.

Substrate temperature	298°C
BEP ratio (Se/Zn)	2
Growth rate	0.5 $\mu\text{m}/\text{hour}$
Epilayer thickness	2 μm

RHEED patterns were monitored extensively during oxide removal and during growth to identify the surface conditions. The detailed oxide removal procedure will be explained later in Chapter 4. After growth, the samples were removed from the MBE system and extensively analyzed using the various characterization techniques discussed below.

Characterization Techniques

High Resolution X-Ray Diffraction

High resolution x-ray diffraction (HRXRD) was used to analyze the homoepitaxial ZnSe epilayers as well as the as-received ZnSe wafers. A Philips diffractometer, Model HR1, equipped with a Bartels four-Ge crystal monochromator [63] was used for this analysis. The germanium crystals have (110) crystalline surfaces and are set for either 220 or 440 reflections for the $\text{CuK}\alpha$ radiation (acceleration voltage and current : 40 kV and 40 mA, respectively). The four-crystal monochromator produces a nearly monochromatic x-ray beam with a very low divergence ($\Delta\theta$) and low wavelength spreading ($\Delta\lambda/\lambda$). Analysis using such a system is generally regarded as high resolution x-ray diffraction. When Ge(220) is used for incident beam optics, $\Delta\theta$ is 12 arcseconds and $\Delta\lambda/\lambda$ is about 2.3×10^{-5} . In this study, a triple axis system was extensively used as a diffracted beam optic system. This system will be outlined briefly below as will basic theoretical concepts for the rocking curve measurements.

Triple axis diffracted beam optic system

The main feature of the triple axis system is its ability to distinguish between the effects of lattice misorientations ($\Delta\phi$) and lattice strain or mismatch ($\Delta a/a$) on the diffraction profile (rocking curve), allowing both substrates and epilayers to be more fully characterized [64, 65]. Both double axis and triple axis optics systems are illustrated in Figure 2.6 (a) and (b), respectively; they are also known as HR 5-crystal optics (or “receiving slit mode”) and HR 7-crystal optics depending upon the number of reflections involved, respectively. In the case of receiving slit mode, an open-ended detector (no slits in front of detector) was used resulting in acceptance angle of about 2 degrees. In the case of triple axis mode, an analyzer crystal consisting of a U-shaped germanium crystal (Bonse-Hart collimator) was positioned in front of the detector. It was mounted so that the $\text{CuK}\alpha_1$ radiation underwent two (220) reflections before entering the detector resulting in an acceptance angle of around 12 arcseconds. This extremely narrow acceptance angle allowed the separation of lattice parameter and misorientation contributions to diffraction peak broadening. Therefore, the alignment of the analyzer crystal with respect to the beam optics was extremely critical.

Rocking curves

A rocking curve of a sample consists of the intensity of the x-ray beam reflected off the sample versus the angle (θ) through which the sample is rotated (“rocked”) assuming the intensity of the reflected x-ray beam is detected by a stationary detector and the angle of rotation includes the Bragg angle (θ_B) of a particular crystallographic plane

[66]. To explain in detail, a schematic of the x-ray configuration used to obtain rocking curves for this study is shown in Figure 2.2 (a). As shown in the Figure, ω is the angle between the optical axis of the x-ray source and crystal surface plane. Two-theta (2θ) is the angular position of the detector relative to the sample optical axis.

Two different types of rocking curves were recorded in this study, namely, a conventional ω rocking curve and an $\omega/2\theta$ (omega/two-theta) rocking curve. During $\omega/2\theta$ rocking curve measurement both the detector (2θ) and the sample are rotated with the detector moving at twice the angular velocity of the sample. According to Fewster [67-69], ω rocking curves can reveal the mosaic structure spread (explained below) whereas the $\omega/2\theta$ rocking curve is sensitive to the lattice parameter variation or strain.

Crystal mosaicity can result from the segregation of defects enclosing regions of perfect crystallinity (mosaic block) and the mosaic spread is the angular distribution of tilts between these regions [66, 68]. Therefore, a mosaic block which is misoriented relative to θ by an angle $\delta\theta$ will satisfy Bragg's law at $(\theta+\delta\theta)$ leading to broadening of the ω rocking curve [65]. Lattice parameter measurements using the $\omega/2\theta$ rocking curve is well established and explained [70, 71]

Transmission Electron Microscopy

The as-received ZnSe substrates and selected homoepitaxial ZnSe epilayer samples were analyzed by cross-sectional and plan-view transmission electron microscopy (XTEM and PTEM) using a JEOL 200CX transmission electron microscope.

TEM analyses were conducted using the various reflections available on (011) and (001) zones. Sample preparation techniques for XTEM and PTEM analyses are described below.

XTEM sample preparation procedure

Since the ZnSe is relatively soft material, careful sample preparation is needed. First, the homoepitaxial ZnSe samples were thinned mechanically on the substrate side to a thickness of about 0.3 mm. Then, a piece of 0.4 mm thick GaAs wafer material was glued to the substrate side of the sample using M600 Bond epoxy resin in order to give mechanical strength during subsequent dicing. This (ZnSe+GaAs) sample was then heated for an hour at 120°C in a conventional oven to cure the epoxy. After curing, the (ZnSe+GaAs) sample was cut into 11 mil thick strips using a dicing saw. The epilayer surfaces of two of the strips were then coated with M600 Bond epoxy and joined “face to face”. The bonded strips were then cured in the oven at 120°C for an hour. These strips were polished from the dicing thickness down to a thickness of about 50 μm using silicon carbide grinding paper. A copper ring was then bonded to the thinned specimen using M600 bond to provide mechanical stability after which the specimen was thinned further in a Gatan ion milling machine using the sputtering action of two Ar^+ ion guns at a gun voltage of 3 kV and a gun current of 0.8 mA until a small hole developed.

PTEM Sample Preparation Procedure

The indium on the substrate side of the sample was first removed by mechanical polishing. The sample was then cleaved into square pieces in such a way that the diagonal length of the square was about 3 mm. Then, the sample was thinned down from the substrate side to a thickness of about 1 mm. A copper ring was bonded to the thinned specimen after which the sample was carefully polished further to a thickness of about 50 μm . The sample was then ion-milled until a tiny hole was obtained.

Etch-pit density measurement

The as-received ZnSe wafers and selected homoepitaxial samples were sent to the 3M Company for etch-pit density measurements in order to estimate the stacking fault density directly. It is known that each etch-pit corresponds to a stacking fault and since the size of an etch-pit related to stacking fault is significantly larger than that related to a dislocation, stacking faults and dislocations can be distinguished. An etching solution of bromine-methanol was used for the EPD analysis [72].

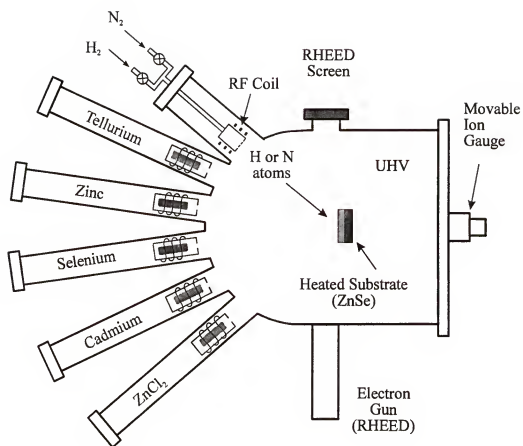


Figure 2.1 Schematic of custom-designed molecular beam epitaxy growth chamber.

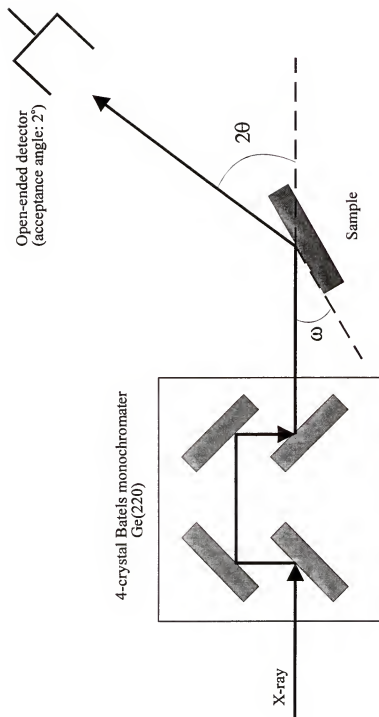


Figure 2.2 (a) Five-crystal configuration of HRXRD used in this study

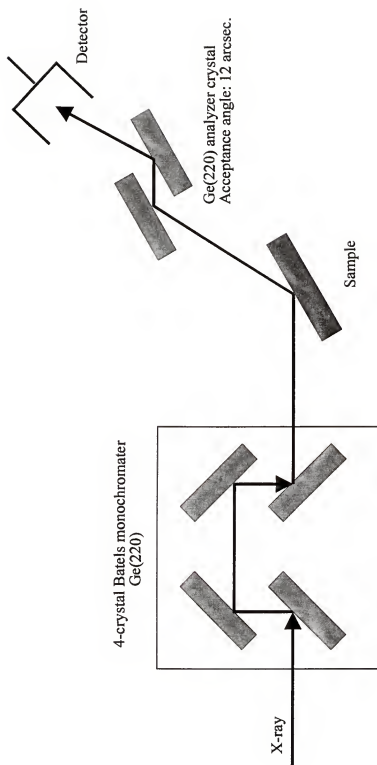


Figure 2.2 (b) Seven-crystal configuration of HRXRD used in this study

CHAPTER 3 CHARACTERIZATION OF SUMITOMO ZINC SELENIDE WAFERS

Sumitomo ZnSe Wafers

The ZnSe substrates used in this study were purchased from Sumitomo Electric Industries, Ltd. and were (001) oriented ZnSe wafers which were sliced from a single crystal ingot produced by what Sumitomo terms a “solid growth method”. In their method, a high purity polycrystalline ZnSe ingot is transformed into a single crystal ingot by annealing the polycrystalline ingot at 1100 °C in an overpressure of Se. Apparently, abnormal grain growth occurs as a result of Se diffusion through grain boundaries and single crystal growth can be affected by appropriate application of stress during the process. The Sumitomo ZnSe wafers have been characterized in this study using HRXRD, AFM, PL and TEM analyses and these results will be presented in this chapter.

A total of 30 ZnSe wafers (approximately 1 cm square and having a thickness of 1 mm) were received in four separate batches (Batch 1 through Batch 4). The batches were supplied to us at different times beginning with Batch 1 and ending for this study with Batch 4. The wafers have been characterized with reference to their respective batch numbers. The sample numbers within each batch are as indicated below:

Batch 1: KR12261, KR12262, KR12263 and KR12264
Batch 2: KR13447, KR13448, KR13450, KR13452, KR13453
Batch 3: KR14370 and KR14371
Batch 4: KR15101 through KR15118

Characterization

HRXRD Analysis

HRXRD analysis was performed on all wafers in Batch 1, Batch 2, and Batch 3 and two randomly selected wafers (KR15103 and KR15108) from Batch 4. The analysis was performed using the 5-crystal configuration with open-ended detector. The full width at half maximum (FWHM) values for the (004) reflection rocking curves for Batch 1 through Batch 3 are presented in Table 3.1. Also, representative rocking curves are illustrated in Figures 3.1-3.4. As can be seen from the FWHM data concerning samples in Batch 1 and Batch 2, the rocking curve linewidths are slightly smaller in Batch 2 than in Batch 1, although there appears to be significant variations in the data within each batch. The wafers in Batch 1 typically exhibited asymmetric rocking curves as illustrated in Figure 3.1. In contrast, the wafers of Batch 2 exhibited symmetric rocking curves as illustrated in Figure 3.2. Two wafers in Batch 3 exhibited quite different FWHM values. However, both wafers exhibited symmetric rocking curves as illustrated in Figures 3.3 and 3.4.

HRXRD analysis was performed on two ZnSe wafers (KR15103 and KR15108) from Batch 4, the batch most recently obtained from Sumitomo; the FWHM values determined for the (004) and (224) reflections are presented in Table 3.2. Representative rocking curves are also illustrated in Figures 3.5-3.8. As can be seen from Table 3.2, the two samples exhibited almost identical FWHM values. These FWHM values (16.2 arcsec.) are the smallest observed so far from the Sumitomo ZnSe wafers.

Table 3.1 FWHM values determined from the (004) reflection rocking curves. 5-crystal HRXRD optics was employed to record rocking curves.

Batch	Sample ID	Reflection	FWHM (arcsec.)	Remark
Batch 1	KR12261	(004)	21.6	Figure 3.1
	KR12262	(004)	19.8	
	KR12263	(004)	27.0	
	KR12264	(004)	21.0	
Batch 2	KR13447	(004)	20.4	Figure 3.2
	KR13448	(004)	20.1	
	KR13450	(004)	17.4	
	KR13452	(004)	17.3	
	KR13453	(004)	20.0	
Batch 3	KR14370	(004)	28.8	Figure 3.3
	KR14371	(004)	19.8	Figure 3.4

Table 3.2 HRXRD rocking curve data for KR15103 and KR15108 (Batch 4) using 5-crystal optics.

Sample ID	Reflection	FWHM (arcsec.)	Remark
KR15103	(004)	16.2	Figure 3.5
"	(224)	25.2	Figure 3.6
KR15108	(004)	16.2	Figure 3.7
"	(224)	25.9	Figure 3.8

Table 3.3 HRXRD rocking curve data for KR15103 (Batch 4) using 7-crystal optics.

In this case, two different scan axes, namely, ω and $\omega/2\theta$ were used to record the rocking curves.

Scan Axis	Reflection	FWHM (arcsec.)	Remarks
ω	(004)	7.74	Figure 3.9
$\omega/2\theta$	(004)	14.8	Figure 3.10
ω	(224)	13.0	Figure 3.11
$\omega/2\theta$	(224)	23.4	Figure 3.12

Asymmetric reflections were recorded using diffraction from the (224) planes. Rocking curves collected from asymmetric reflection planes have contributions from both the parallel and perpendicular direction. Therefore, as can be seen in Table 3.2, the FWHM of asymmetric rocking curve is usually larger than that of symmetric rocking curves which have only one contribution from the vertical direction.

Rocking curves of the (004) and (224) reflections were recorded for sample KR15103 from Batch 4 using an analyzer crystal (7-crystal optics). Using the 7-crystal optics, it is possible to separate lattice plane spacing versus mosaic spread contributions to rocking curve broadening as discussed in Chapter 2. Table 3.3 shows the FWHM values determined for the (004) and (224) reflections using both the ω -scan and the $\omega/2\theta$ -scan axes. The FWHM value (7.74 arcsec.) of the ω rocking curve of the (004) reflection recorded using an analyzer crystal is less than one half of the FWHM value (16.2 arcsec.) of the rocking curve determined using a receiving slit (open-ended) mode whereas the FWHM value (14.8 arcsec.) of the $\omega/2\theta$ rocking curve of the (004) reflection recorded using an analyzer crystal is nearly the same as that of the rocking curve determined using receiving slit (open-ended) mode. The asymmetric scan also exhibited the same tendency. Therefore, these data clearly show that the rocking curve broadening observed in the receiving slit mode was mostly attributed to lattice strain, not mosaicity, because the ω rocking curves reveal mosaicity while $\omega/2\theta$ rocking curves reveal strain or lattice parameter spread as previously reviewed. It is believed that the strain in the substrate is attributed to defects in the material such as dislocations and stacking faults.

In order to assess the quality of the Sumitomo ZnSe wafers, rocking curves for a GaAs wafer obtained from American Xtal Technology (AXT) were recorded. The etch-pit density of this GaAs wafer was on the order of 10^3 cm^{-2} . Table 3.4 shows the FWHM values determined for the (004) and (224) reflections using both ω -scan and $\omega/2\theta$ -scan axes.

Table 3.4 HRXRD rocking curve data for AXT-GaAs wafer using both 5- and 7-crystal optics. Both ω and $\omega/2\theta$ scan axes were used to record the rocking curves.

Scan Axis	Reflection	FWHM (arcsec.)	Diffracted Beam Optics	Remark
ω	(004)	15.3	5-crystal	Figure 3.13
ω	(004)	6.5	7-crystal	Figure 3.14
$\omega/2\theta$	(004)	14.4	7-crystal	Figure 3.15
ω	(224)	23.4	5-crystal	Figure 3.16
ω	(224)	7.5	7-crystal	Figure 3.17
$\omega/2\theta$	(224)	23.0	7-crystal	Figure 3.18

As can be seen from the previous tables, the FWHM values for the ZnSe rocking curves are comparable to those of the AXT GaAs wafer. In the case of the GaAs wafer, the rocking curve broadening observed in the receiving slit mode was also mostly due to lattice strain.

AFM Analysis

The surface roughness of the ZnSe wafers was analyzed using an atomic force microscope (NanoScope III; Digital Instruments Inc.) operating in air (see Appendix). In this study, the tapping mode was employed in most cases in order to prevent contamination or damage on the wafer surface. In order to minimize the effects of humidity, temperature and variations in the AFM tip, all samples were scanned at the same time for each batch using the same scanning tip. Also, a reference sample of AXT GaAs was used to compare results taken at different times and to determine the condition of the tip and the instrument.

Tables 3.5, 3.6 and 3.7 show the roughness test results for Batches 1, 2 and 3, respectively. For comparison, the surface roughness of an AXT GaAs wafer was also examined with each batch. Table 3.5 shows the roughness test results for three ZnSe wafers (KR12261, 12262 and KR12264) from Batch 1. This batch of samples had relatively smooth surface morphologies although none were as smooth as the AXT GaAs wafer.

Table 3.6 shows the surface roughness test results for Batch 2. For comparison, the GaAs wafer and KR 12264 from Batch 1 were also examined. As can be seen in Figure 3.21, hillocks about 250 nm in diameter were distributed over the sample surface. The hillock density is about $7 \times 10^7 \text{ cm}^{-2}$. Other samples (KR13448, KR13450, KR13452 and KR13453) also contained these hillocks. The hillocks were not observed on the surfaces of Batch 1 wafers (KR12261-KR12264). In order to find the true surface roughness for Batch 2 samples, 500 nm x 500 nm areas were selected (see Table 3.6) that

did not contain hillocks. Table 3.6 shows the mean RMS values of the five Batch 2 samples and KR12264 from Batch 1. The samples in Batch 2 appeared to have rougher surfaces (3~4 times rougher) compared with those of the samples from Batch 1. Information from Sumitomo indicated that the Batch 2 samples had been polished twice and, therefore, the increase in surface roughness may have been due to the poor repolishing of the samples.

Table 3.7 and the corresponding figures indicate the roughness test results on Batch 3. The roughness of the samples in Batch 3 was similar to that of the Batch 1 samples but the Batch 3 sample surfaces contained hillocks. Sample KR14370 was also scanned using the contact mode (Figure 3.23). Scans were made in several 500 nm x 500 nm hillock-free regions to find actual roughness(see Table 3.7). The hillocks that were observed on earlier samples were seen again in this case although the hillocks were determined to be much smaller under the contact mode scan. Therefore, the size of the hillocks determined by the tapping mode is not real. The average width and height of the hillocks determined by the contact mode are 141 nm and 3.5 nm, respectively. The hillock density was about $4 \times 10^7 \text{ cm}^{-2}$.

Table 3.8 shows the roughness test results on two ZnSe wafers (KR 15103 and KR 15108 from Batch 4. These samples exhibited almost identical surface roughnesses (0.16 nm). This batch of samples had the smoothest surface morphologies (as smooth as that of the AXT GaAs wafer). Also, the hillock density was greatly reduced.

Table 3.5 Surface roughness test results for Batch 1.

Sample	RMS* (nm)	Remarks
KR 12261	0.292	-
KR 12262	0.212	-
KR12264	0.185	Figure 3.19
GaAs	0.139	Figure 3.20

Table 3.6 Surface roughness test results for Batch 2. For roughness calculations, hillock-free areas were scanned.

Sample	No. of 500 nm x 500 nm regions checked for roughness without hillocks	Mean RMS* (nm)	Remarks
KR 13447	13	0.541	Figure 3.21
KR 13448	34	0.721	
KR13450	26	0.677	
KR13452	20	0.771	
KR13453	30	0.541	
KR12264	6	0.185	
GaAs	1	0.135	

* Mean RMS : An average of RMS values from three 1 μm scans (without hillocks on surface)

Table 3.7 Surface roughness test results for Batch 3. For roughness calculations, hillock-free areas were scanned.

Sample	No. of 500 nm x 500 nm regions checked for roughness without hillocks	Mean RMS (nm)	Hillock Density (cm^{-2})	Remarks
KR14370	15	0.216	4×10^7	Figure 3.22
KR14371	15	0.221	4.4×10^7	
GaAs	6	0.133	-	
KR14370	10	0.260	4.8×10^7	By contact mode Figure 3.23

Table 3.8 The surface roughness test results for KR15103 and KR15108 from Batch 4.
For roughness calculations, hillock-free areas were scanned.

Sample	No. of 1 μm x 1 μm regions checked for roughness without hillocks	Mean RMS*(nm)	Hillock Density (cm^{-2})	Remarks
KR15103	29	0.169	$\sim 10^7$	Figure 3.24 Figure 3.25
KR15108	22	0.162	$\sim 10^7$	Figure 3.26 Figure 3.27
GaAs	1	0.165	-	

* Mean RMS : An average of RMS values from 1 μm x 1 μm regions (without hillocks on surface)

Photoluminescence Analysis

Low-temperature photoluminescence (PL) spectra were recorded from KR 12261 from Batch 1 (Figures 3.28(a) and (b)). Relatively strong neutral donor-bound exciton emission, I_2 , and ionized donor-bound exciton emission, I_3 , were observed at 2.7972 eV and 2.7947 eV, respectively. The free exciton emission, E_x , at 2.801 eV was also detected. However, a large unidentified defect-related emission was observed centered at 2.5358 eV.

PL spectra from KR 13447 (Batch 2) were also recorded (Figures 3.29 a, b, and c). An extremely strong, sharp, neutral acceptor-bound exciton emission, I_1^d , having a FWHM of 1 meV was observed at 2.7830 eV (Figure 3.29 (a)). The I_1^d line exhibited strong phonon replicas (I_1^d -1LO, I_1^d -2LO, and I_1^d -3LO shifted by about 32 meV). The I_1^d emission is believed to be associated with native defects such as zinc vacancies (V_{zn}) [48]. Very weak free exciton (E_x) and neutral donor-bound exciton (I_2) emissions were observed at 2.802 eV and 2.797 eV, respectively (Figure 3.29 (b)). A small but significant unidentified defect-related emission (Figure 3.29 (c)) was found at 2.5402 eV which was very large in the previous sample KR12261. Therefore, it appears that the crystalline quality of the Batch 2 samples was improved over that of the Batch 1 samples.

Figures 3.30 (a) and 3.30 (b) illustrate the PL spectra recorded from sample KR14371 from Batch 3. Overall optical quality was improved for this batch compared with samples from the previous batches. The dominant emission was a neutral acceptor-bound exciton (I_1^Y) at 2.7926 eV which is believed to be associated with Na acceptor

impurities (Figure 3.30 (a)). However, I_1^d and its phonon replicas were still strong. Weak but significant free exciton (E_x) and neutral donor-bound exciton (I_2) emissions were also observed at 2.802 eV and 2.797 eV, respectively. However, the most important feature of sample KR14371 is the elimination of the deep level emissions at around 2.5 eV that were observed for samples from previous batches (Figure 3.30 (b)).

Low-temperature photoluminescence (PL) spectra recorded from KR 15103 in Batch 4 are shown in Figures 3.31(a) and 3.31(b). In this case, the dominant emissions were neutral donor-bound exciton emission (I_2) and free exciton emission (E_x) observed at 2.7964 and 2.8002 eV, respectively. Also, a donor-acceptor pair (DAP) emission (2.707 eV) with its phonon replicas were observed. Absent from these spectra are the I_1^d emission and its phonon replicas. Therefore, the PL spectra from Batch 4 samples are greatly improved relative to those of samples in previous batches.

TEM Analysis

Both plan-view (PTEM) and cross-sectional transmission electron spectroscopy (XTEM) specimens were prepared and examined. Figure 3.32 illustrates the TEM micrographs for KR12261 (Batch 1) indicating the presence of micro-twins, stacking faults and dislocations. The dislocation density is about 10^7 cm^{-2} . Figure 3.33 shows the TEM images of sample KR 13447 from Batch 2. The dislocation density is about the same as in the previous sample ($\sim 10^7 \text{ cm}^{-2}$); however, in this case, micro-twins were not observed.

PTEM analysis was performed on KR15103 from Batch 4. The dislocation density was determined to be in the low 10^5 cm^{-2} range. Figure 3.34 shows the TEM images of sample KR 15103. No other types of defects were observed. A 5 mm x 5 mm sample from KR15103 was cleaved and sent to 3M for etch-pit density analysis. It is known that each etch-pit corresponds to a stacking fault. It was found that the stacking fault density of KR15103 (Batch 4) was about $6.9 \times 10^4 \text{ cm}^{-2}$.

Summary

Based on the data that we have collected thus far from the Sumitomo ZnSe wafers, a significant improvement has been achieved over time with regard to ZnSe wafer quality. Specifically, ZnSe wafers in Batch 4 exhibited the narrowest rocking curve linewidth and the smoothest surface morphologies (as smooth as that of the AXT GaAs wafer). However, these wafers still contain impurities and dislocations (low 10^5 cm^{-2} range) based on low-temperature PL and TEM analyses. Also, hillocks of an unknown source were observed on ZnSe wafer surfaces although the hillock density was greatly reduced in Batch 4 samples.

The ZnSe wafers in Batch 4 exhibited, thus far, the best quality received from Sumitomo and, in this study, all homoepitaxial growth was performed on ZnSe wafers from Batch 4.

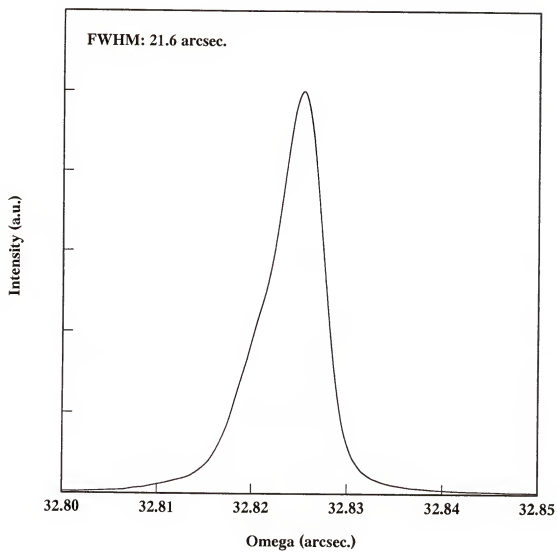


Figure 3.1 X-ray rocking curve of (004) reflection recorded from KR12261 (Batch 1)

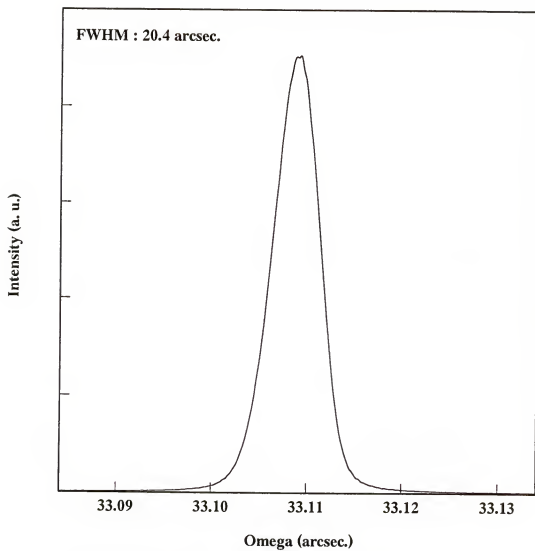


Figure 3.2 X-ray rocking curve of (004) reflection recorded from KR13447 (Batch 2).

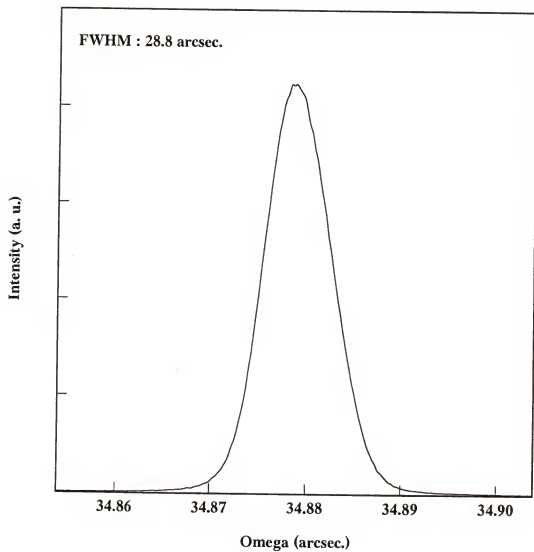


Figure 3.3 X-ray rocking curve of (004) reflection recorded from KR14370 (Batch 3).

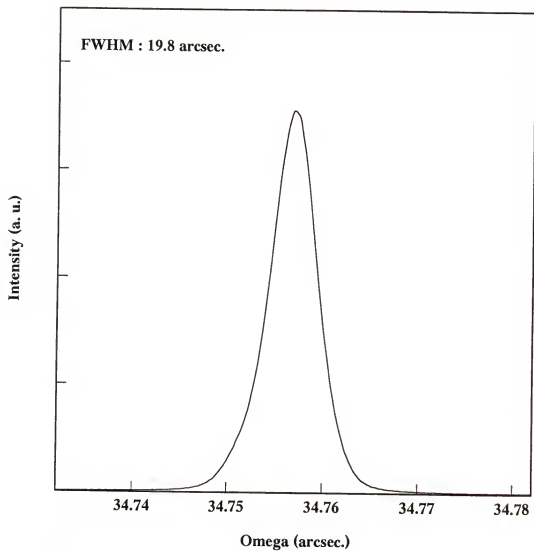


Figure 3.4 X-ray rocking curve of (004) reflection recorded from KR14371(Batch 3)

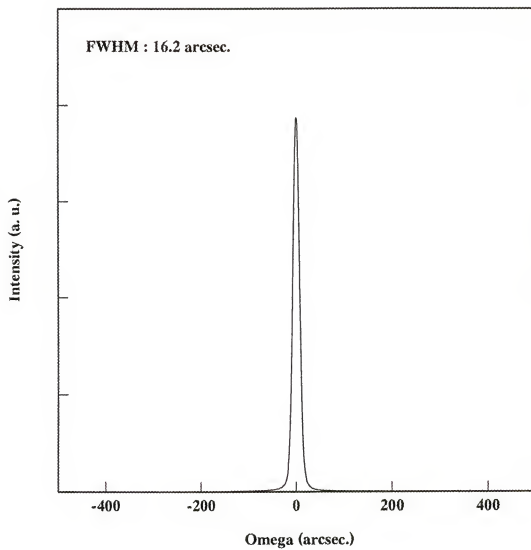


Figure 3.5 X-ray rocking curve of (004) reflection obtained from KR15103 (Batch 4).

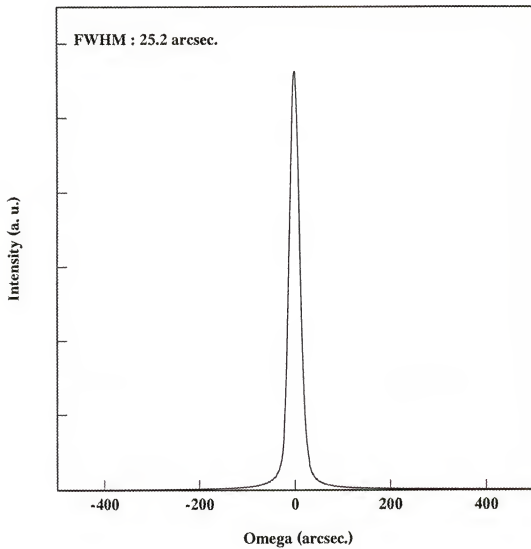


Figure 3.6 X-ray rocking curve of (224) reflection obtained from KR15103 (Batch 4).

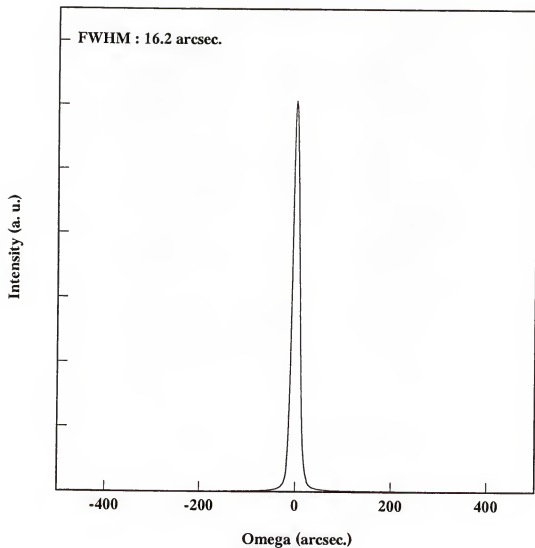


Figure 3.7 X-ray rocking curve of (004) reflection obtained from KR15108 (Batch 4).

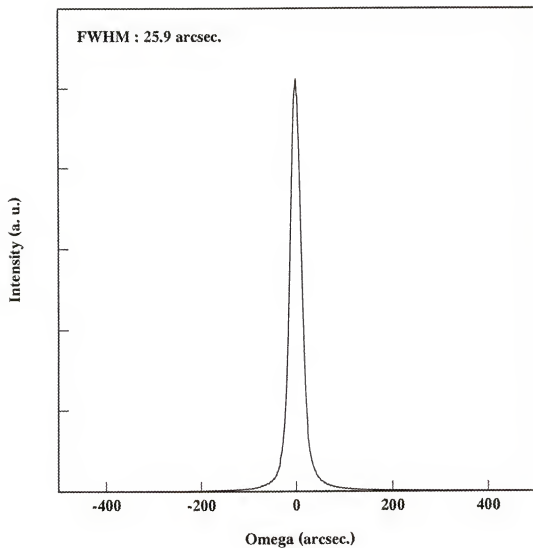


Figure 3.8 X-ray rocking curve of (224) reflection obtained from KR15108 (Batch 4).

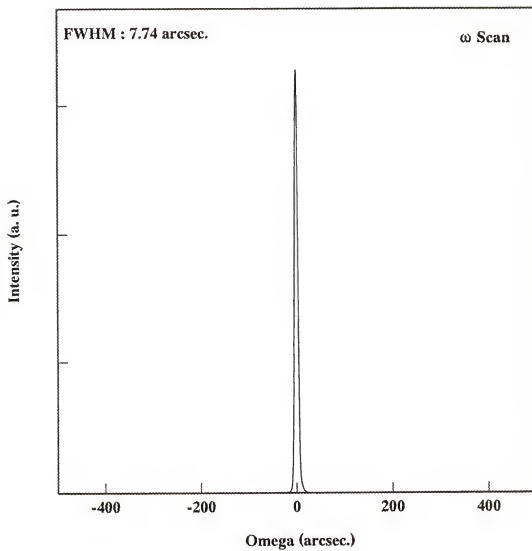


Figure 3.9 X-ray rocking curve of (004) reflection obtained from KR15103 (Batch 4) using analyzer crystal.

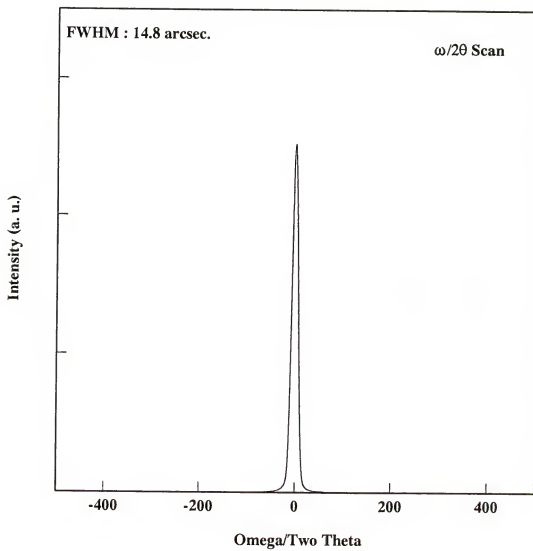


Figure 3.10 X-ray rocking curve of (004) reflection obtained from KR15103 (Batch 4) using analyzer crystal.

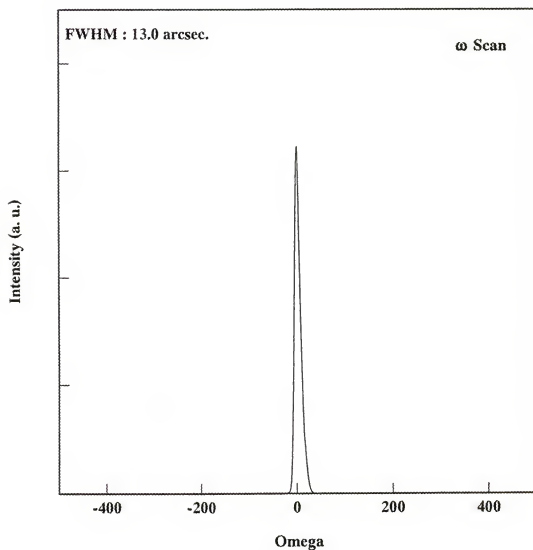


Figure 3.11 X-ray rocking curve of (224) reflection obtained from KR15103 (Batch 4) using analyzer crystal.

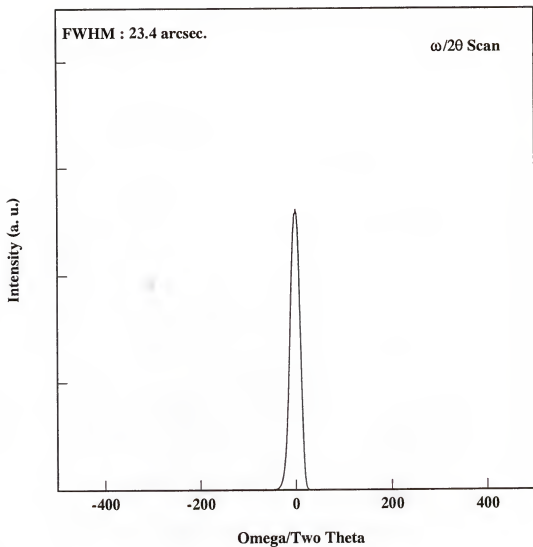


Figure 3.12 X-ray rocking curve of (224) reflection obtained from KR15103 (Batch 4) using analyzer crystal.

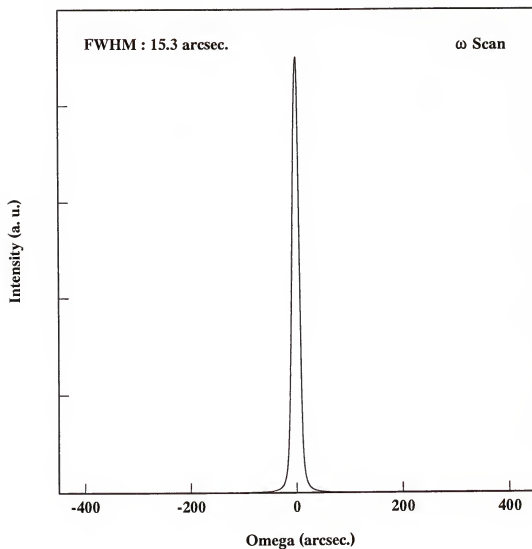


Figure 3.13 X-ray rocking curve of (004) reflection obtained from the AXT GaAs wafer.

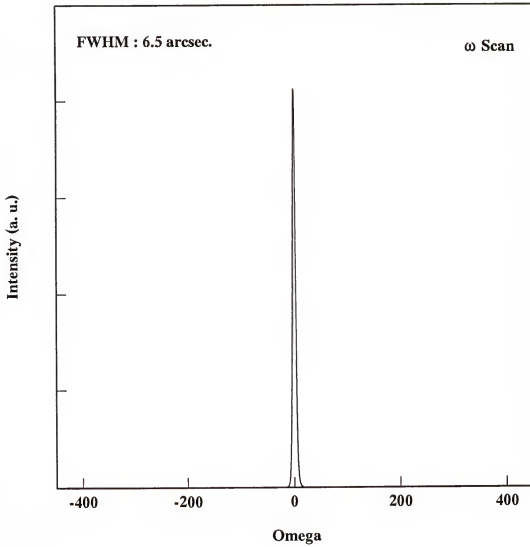


Figure 3.14 X-ray rocking curve of (004) reflection obtained from the AXT GaAs wafer using analyzer crystal.

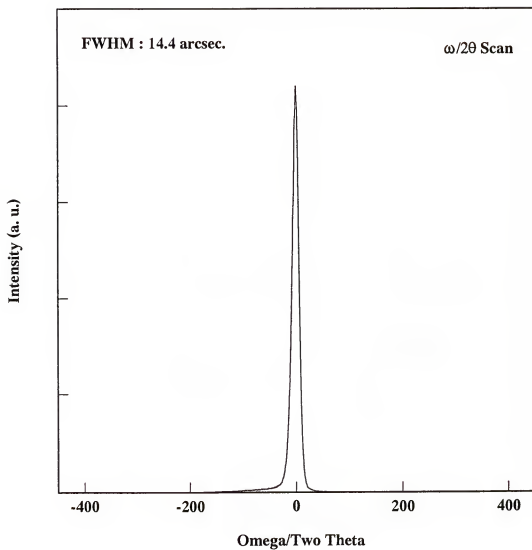


Figure 3.15 X-ray rocking curve of (004) reflection obtained from the AXT GaAs wafer using analyzer crystal.

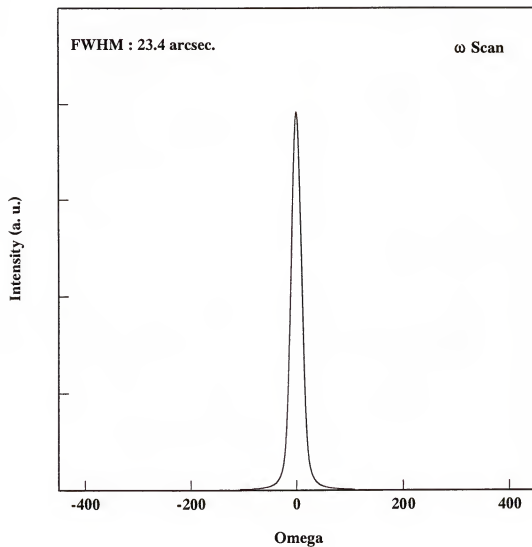


Figure 3.16 X-ray rocking curve of (224) reflection obtained from the AXT GaAs wafer.

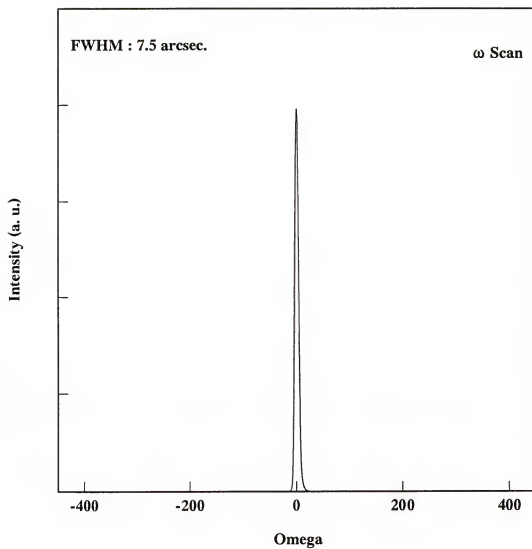


Figure 3.17 X-ray rocking curve of (224) reflection obtained from the AXT GaAs wafer using analyzer crystal.

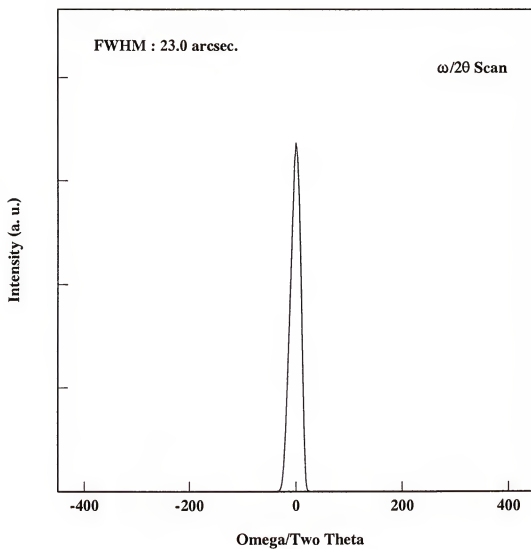


Figure 3.18 X-ray rocking curve of (224) reflection obtained from the AXT GaAs wafer using analyzer crystal.

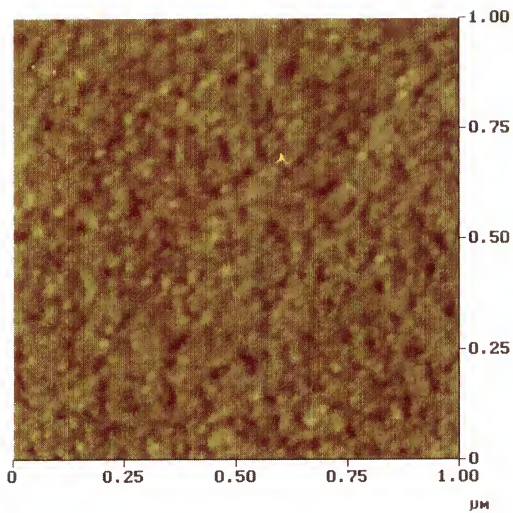


Figure 3.19 AFM image for KR12264 from Batch 1 using tapping mode.

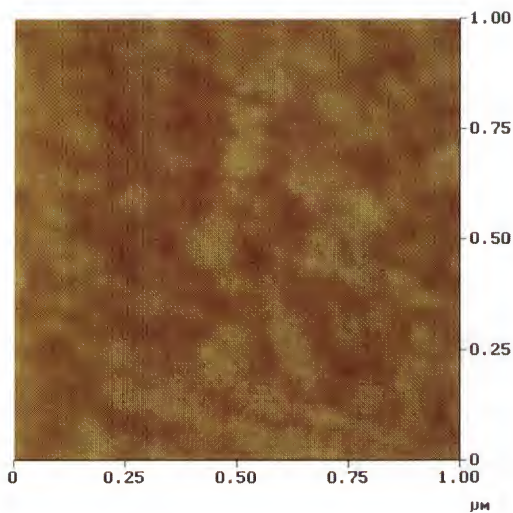


Figure 3.20 AFM image for AXT GaAs using tapping mode.

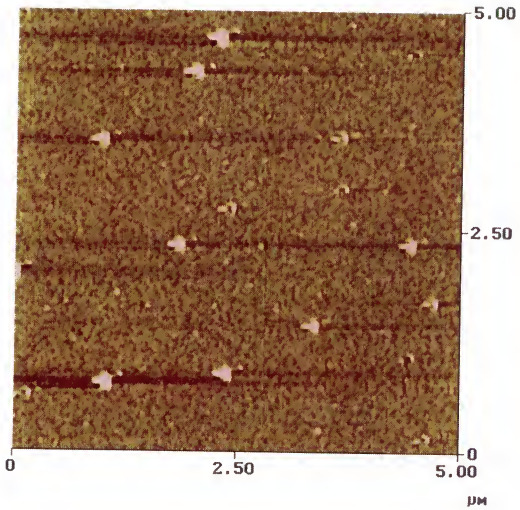


Figure 3.21 AFM image for KR13447 from Batch 2 using tapping mode.

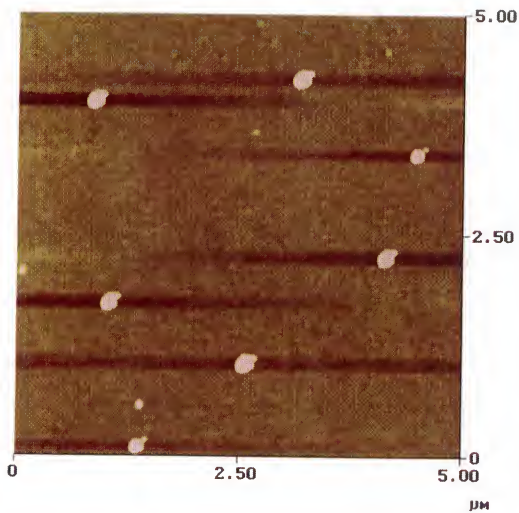


Figure 3.22 AFM image for KR14370 from Batch 3 using tapping mode. ($1\ \mu\text{m} \times 1\ \mu\text{m}$)

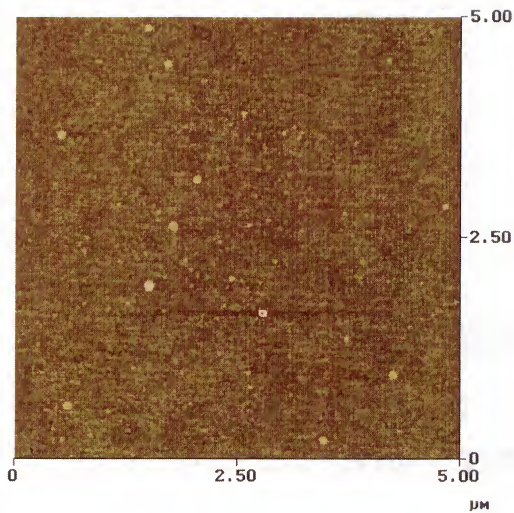


Figure 3.23 AFM image for KR14370 from Batch 3 using contact mode

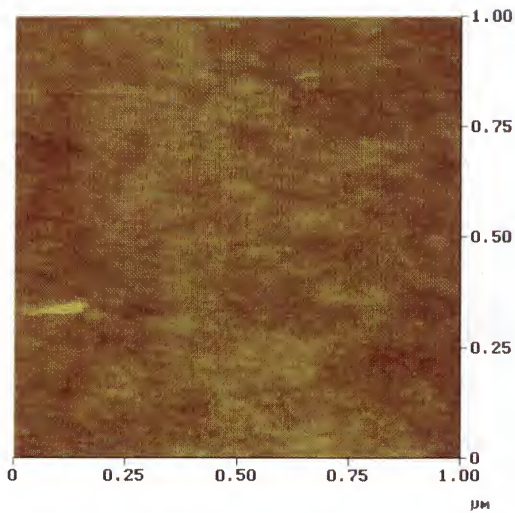


Figure 3.24 AFM image for KR15103 from Batch 4 using tapping mode. ($1\ \mu\text{m} \times 1\ \mu\text{m}$)

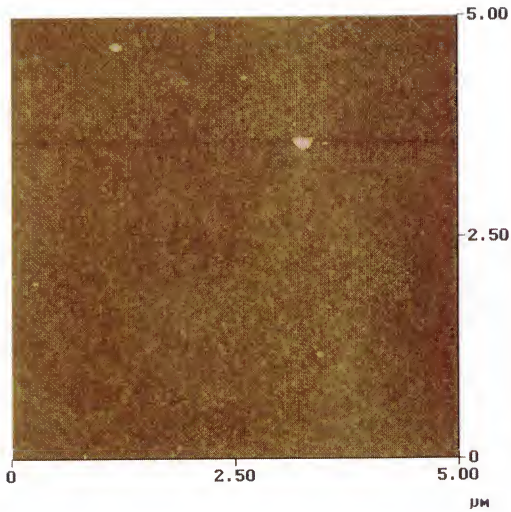


Figure 3.25 AFM image for KR15108 from Batch 4 using tapping mode. Hillocks are shown in this figure. ($5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$)

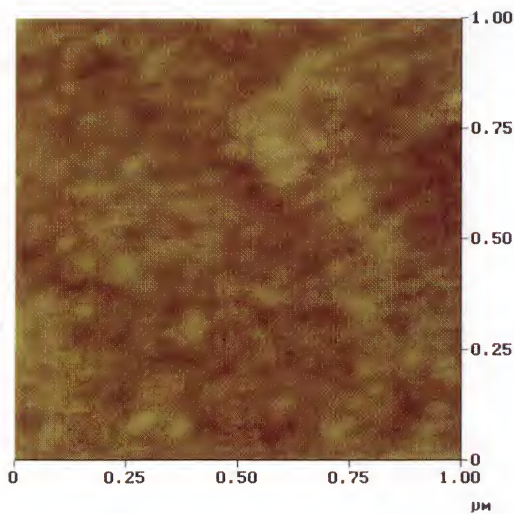


Figure 3.26 AFM image for KR15108 from Batch 4 using tapping mode. ($1\ \mu\text{m} \times 1\ \mu\text{m}$)

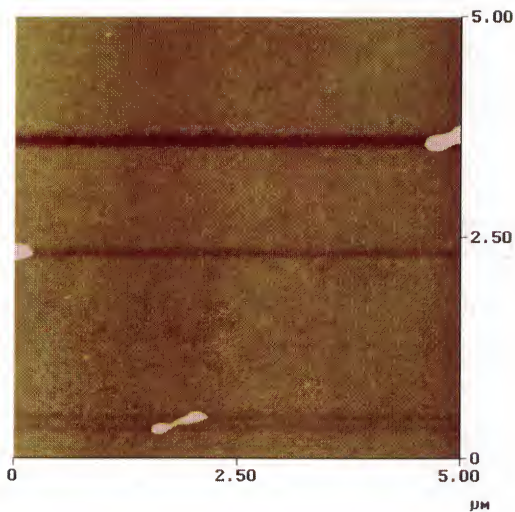


Figure 3.27 AFM image for KR15108 from Batch 4 using tapping mode. Hillocks are shown in this figure. (5 μm x 5 μm)

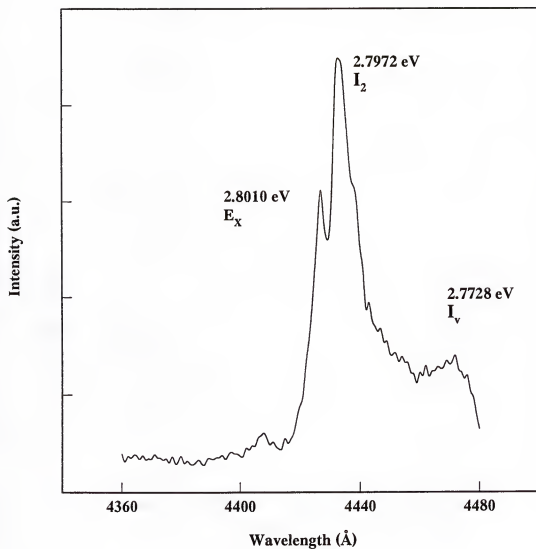


Figure 3.28(a) Low-temperature (6K) PL spectrum recorded from KR 12261 (Batch 1). (High resolution scan)

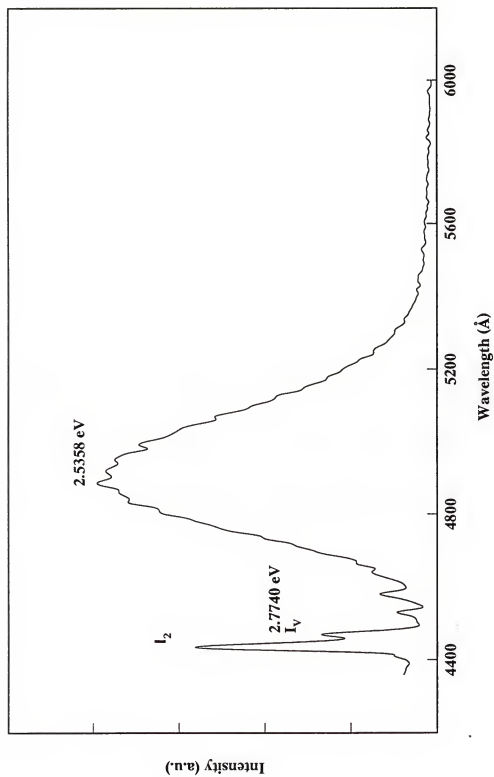


Figure 3.28(b) Low-temperature (6K) PL spectrum recorded from KR 12261 (Batch 1).
(Low resolution scan)

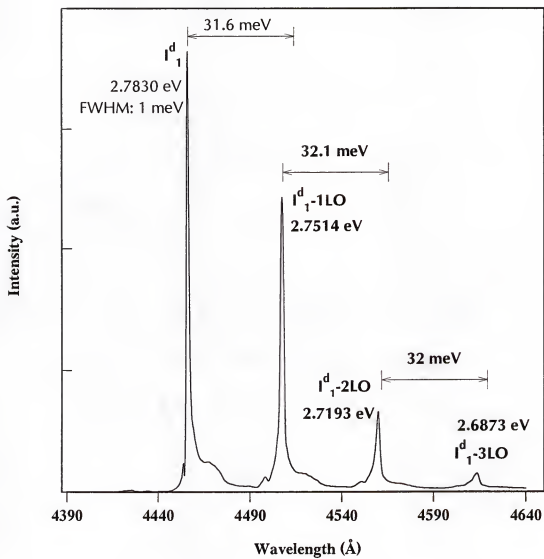


Figure 3.29 (a) Low-temperature (6.5K) PL spectrum recorded from KR 13447 (Batch 2). (High resolution).

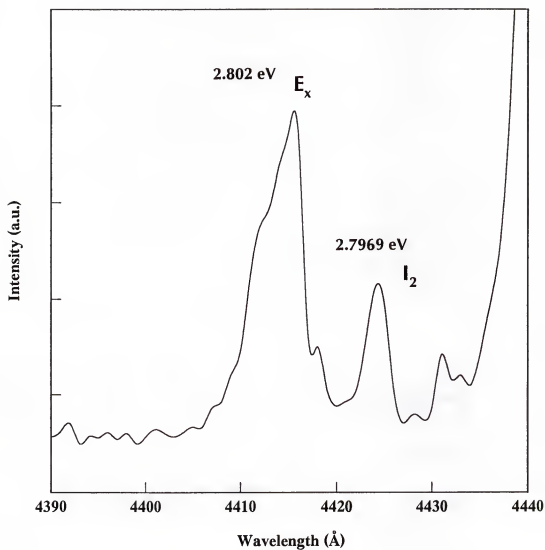


Figure 3.29 (b) Low-temperature (6.5K) PL spectrum recorded from KR 13447 (Batch 2). (Excitonic emission region).

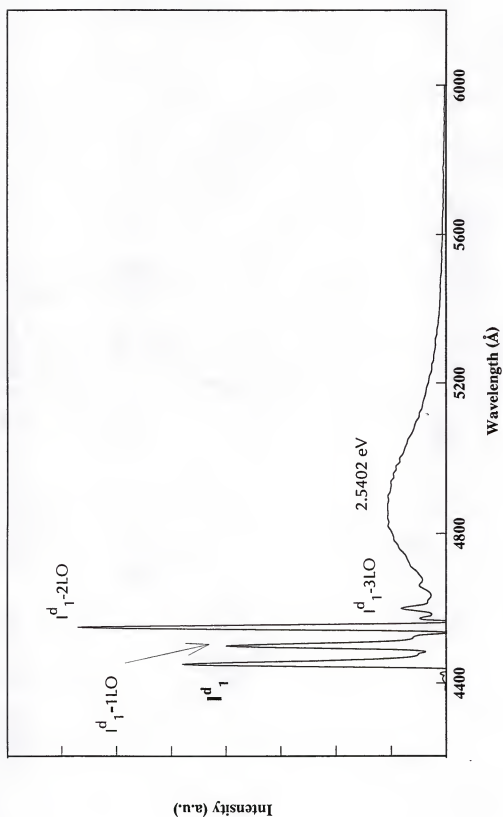


Figure 29(c) Low-temperature (6.5K) PL spectrum recorded from kR13447 (Batch 2).
(Low resolution)

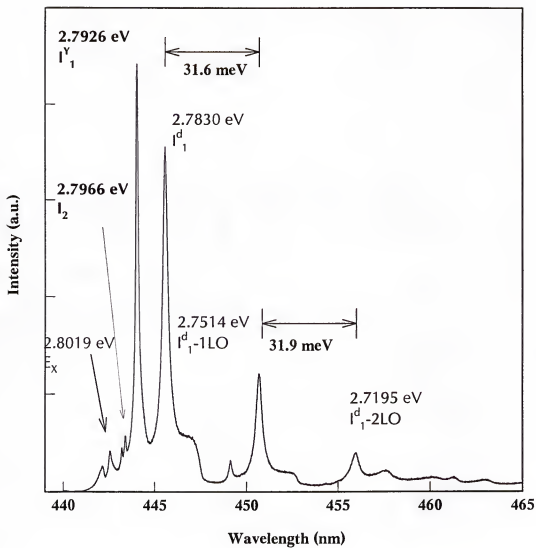


Figure 3.30(a) Low-temperature (26.4K) PL spectrum recorded from KR 14371 (Batch 3). (High resolution)

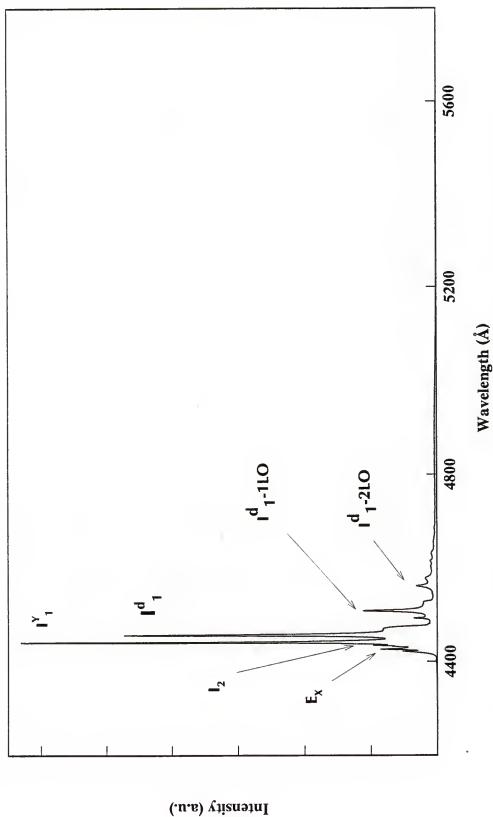


Figure 3.30(b) Low-temperature (24.6K) PL spectrum recorded from KR14371 (Batch 3).
(Low resolution)

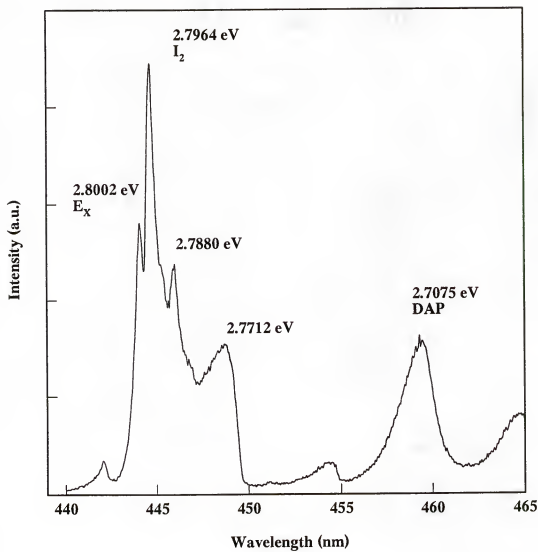


Figure 3.31(a) Low-temperature (23K) PL spectrum recorded from KR 15103(Batch 4). (High resolution)

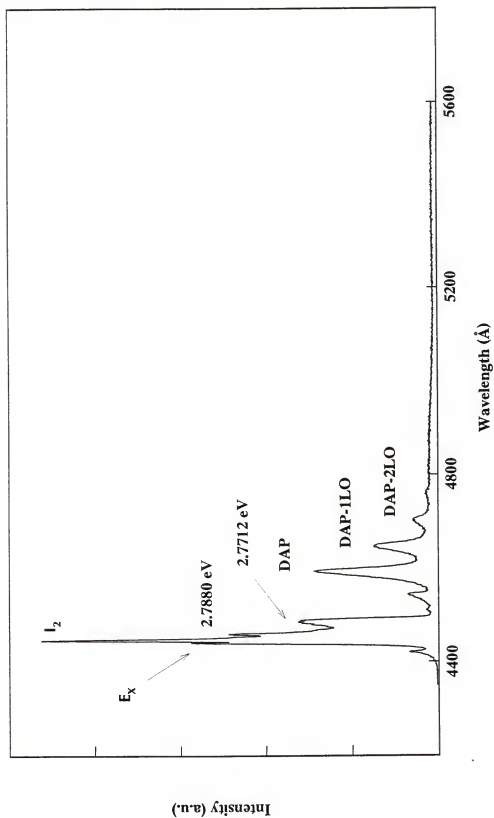


Figure 3.31(b) Low-temperature (23K) PL spectrum recorded from KR15103 (Batch 4).
(Low resolution)

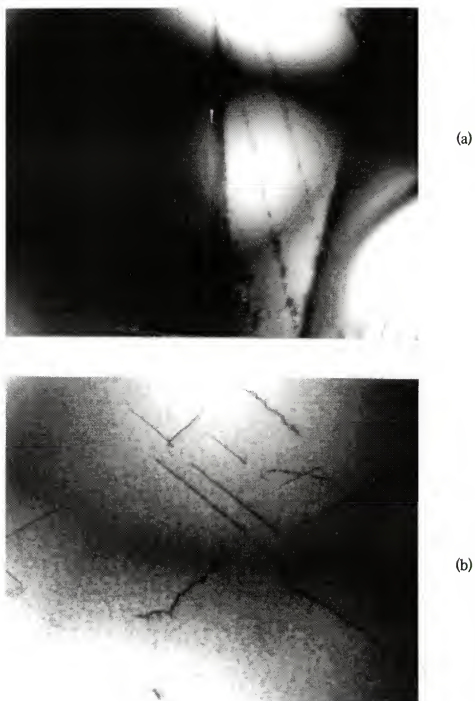
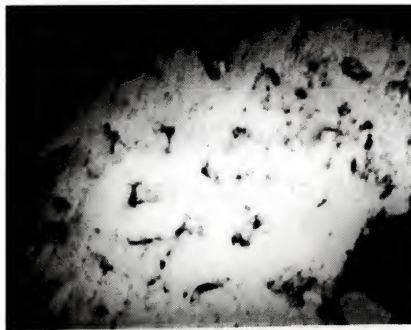
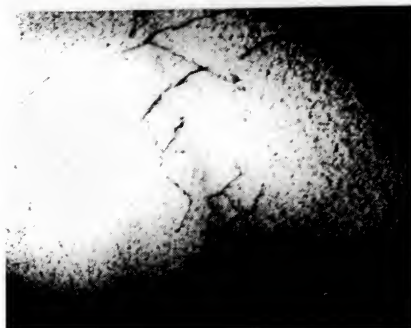


Figure 3.32 TEM micrographs of sample KR12261 (Batch 1); (a) PTEM image of micro-twin (b) XTEM image of defects.



(a)



(b)

Figure 3.33 TEM micrographs of sample KR13447 (Batch 2); (a) PTEM image (b) XTEM image of defects.



Figure 3.34 PTM micrograph of sample KR15103 (Batch 4). One dislocation only was observed from 60 different locations (low 10^5 cm^{-2})

CHAPTER 4 WAFER PREPARATION AND CONVENTIONAL ZnSe HOMOEPITAXIAL GROWTH

Ex-situ Preparation

Introduction

UV-ozone surface treatment is known to be an effective method of removing a variety of contaminants such as organic molecules from substrate surface prior to growth [73]. It is also known that exposure of some materials to UV-ozone can produce a clean oxide "passivated" surface [74-76]. UV-ozone treatment is easy to perform, requires no elaborate equipment, and is a low-temperature process performed in ambient atmosphere.

UV/ozone treatment is primarily the result of photosensitized oxidation processes [75, 76]. The contaminant molecules are excited and dissociated by the absorption of short wavelengths of UV light (253.7 and 184.9 nm) produced by low-pressure Hg discharge lamps in fused quartz envelopes. Simultaneously, atomic oxygen and ozone are produced when O₂ is dissociated by the absorption of UV with a wavelength less than 245.4 nm which corresponds to the energy required to dissociate an O₂ molecule into two ground state O atoms. Atomic oxygen is also produced when ozone is dissociated by the absorption of the UV. The excited contaminant molecules and the free radicals produced by the dissociation of contaminant molecules react with atomic oxygen to form simpler volatile molecules, such as CO₂, H₂O, N₂, etc.

The oxidizing ability of ozone is well known and is surpassed in this ability only by fluorine [76]. Ozone can oxidize most inorganic compounds to their final oxidative state. Usually, for most materials, it is found that UV-ozone cleaning for the minimum time required to obtain a clean surface does not cause a significant amount of oxidation [75]. However, extended exposure to UV-ozone beyond the time required for cleaning has been found to significantly increase the oxide layer thickness. For instance, the native oxide on GaAs is only about 30 Å thick, while UV-ozone treatment can produce a clean and enhanced oxide layer that is 100 to 300 Å thick [76]. In the case of aluminum, whereas the oxide thickness on air exposed surfaces is usually limited to about 50 Å, the oxide thickness was found to be 90 Å after a 10 minute UV-ozone exposure.

On the other hand, it is not known what effect UV-ozone treatment has on the surface morphology of a sample which is particularly important when the sample is to serve as a substrate for epitaxial growth. The quality of epitaxially grown layers is strongly correlated to the substrate surface roughness [43, 77, 78] because a rough surface will result in a higher density of potential nucleation sites and, thus, islands may coalesce before a highly anisotropic shape (epitaxy) has developed [78]. Therefore, it is very important to initiate epitaxial growth on a smooth substrate surface.

In this study, the influence of the *ex-vacuo* substrate preparation procedure (namely, UV-ozone treatment) on ZnSe homoepitaxial layer quality was investigated. The UV-ozone exposure duration was systematically varied and the corresponding surface roughness variation was measured by AFM using the tapping mode (see Appendix). After MBE growth, homoepitaxial epilayers were characterized using PL

and HRXRD to assess the epilayer quality in each case. Finally, the optimum UV-ozone exposure time was chosen based on the characterization results.

UV-ozone treatment of ZnSe substrates

One of the 18 ZnSe wafers from Batch 4 was randomly selected (KR15108) and was cleaved into four pieces, each piece being 5 mm square and having a thickness of 700 μm . Prior to being soldered to a Mo sample holder using molten In (99.9999% pure), these samples were oxidized using a UV-ozone cleaning system manufactured by UVOCS Incorporated. Four different UV-ozone exposure durations and corresponding average RMS values measured by AFM are summarized in Table 4.1.

Table 4.1 UV-ozone exposure durations and corresponding roughness measurement results using AFM.

Sample ID	UV-ozone exposure duration (min.)	Mean RMS (nm)	Standard Deviation
H1	No treatment	0.16	0.028
H2	3	0.21	0.031
H3	6	0.17	0.015
H4	9	0.13	0.019

* Mean RMS: An average of RMS values from at least 10 different 1 μm x 1 μm regions.

A mean RMS value was calculated from RMS values measured from at least ten different 1 μm x 1 μm regions on each sample. It was found that the ZnSe substrate surface roughness was modified by the different UV-ozone exposure durations. Figure 4.1 illustrates the mean RMS vs. UV-ozone exposure duration. As can be seen from the

figure, the as-received sample (H1) had a roughness of 0.16 nm. When the sample was exposed for three minutes, the roughness was increased to 0.21 nm. After six minutes exposure, the roughness decreased to 0.17 nm, nearly the same roughness as that of the as-received sample. Finally, the lowest roughness, 0.13 nm, was exhibited by the sample treated for nine minutes. The 6 minute treated sample (H3) exhibited the lowest standard deviation.

In Situ Oxide Reduction

After the UV-ozone treatment, the samples were loaded into the MBE growth chamber via a separately pumped load lock. In general, prior to epitaxial growth the surface oxide must be removed from the substrate surface to expose the underlying material; this process is often called "cleaning." The conventional method of substrate cleaning is thermal treatment in ultra-high vacuum (either in the growth chamber or in a separate sample preparation chamber). In the thermal treatment, the sample is heated to a temperature high enough to cause desorption of the oxide (or oxides) from the surface. We have found in this work, however, that a combined thermal/H-atom treatment is superior to the conventional thermal method for cleaning ZnSe substrates in that the combined thermal/H-atom method allowed oxide desorption at a lower temperature (300 °C compared with 500 °C) and resulted in a smoother ZnSe surface as evidenced by the RHEED patterns observed from the cleaned surfaces [51]. In this process, the ZnSe wafer was exposed to an atomic hydrogen flux (generated in a remote rf plasma source) as the wafer temperature was increased slowly (over a period of about one hour) from room temperature until a well-defined RHEED pattern was obtained. The sample not

given the UV-ozone treatment and the sample given a three minute UV-ozone treatment developed well-defined RHEED patterns after being exposed to the atomic hydrogen flux for 50 minutes to one hour at 300 °C. The samples given the six and nine minute UV-ozone treatment developed well-defined RHEED patterns after one hour and one and one-half hours exposure to the atomic hydrogen flux at 330 °C, respectively. These results indicate that longer UV-ozone treatments require longer exposure time to the atomic hydrogen flux at higher substrate temperatures to fully desorb the surface oxide from ZnSe. Figures 4.2(a) and 4.2(b) show the RHEED patterns for two orthogonal azimuths recorded from a ZnSe substrate cleaned using the combined thermal/H-atom method. These patterns indicate that the cleaned ZnSe surface has a (1x1) unreconstructed, atomically smooth surface.

MBE Growth of Homoepitaxial ZnSe

After removal of the oxide layer, conventional MBE growth was used to deposit 2 μm -thick epilayers on each of the four substrates by opening both Zn and Se shutter simultaneously. Figures 4.2 (c) and (d) show typical RHEED patterns obtained from a ZnSe homoepitaxial layer in two orthogonal azimuths. The transition from the substrate to the epilayer pattern was imperceptible. An unreconstructed (1x1) RHEED pattern was observed during growth of this homoepitaxial ZnSe layer.

Experimental Results and Discussion

HRXRD Analysis

HRXRD analysis was conducted to determine the optimum UV-ozone exposure time with regard to epilayer quality. X-ray rocking curves were recorded using both the five- and seven crystal configurations. The five-crystal configuration did not provide enough information to assess the quality of the four samples listed in Table 4.1 mainly due to the poor resolution of this configuration. Since the analyzer crystal in the seven-crystal configuration improves the resolution of the x-ray diffractometer, rocking curves recorded using this configuration primarily will be used for this analysis.

The symmetric (004) rocking curves from the four homoepitaxial samples grown on substrates having various UV-ozone exposure times are shown in Figures 4.3-4.6. These rocking curves were collected using the five-crystal optics configuration. As these figures indicate, all of the rocking curves exhibit a shoulder on the left side of the substrate peak. Asymmetric reflections were also measured using diffraction from the (224) planes. The use of asymmetric reflections can reveal information about the in-plane (parallel to the substrate) imperfections of an epilayer. Figures 4.7-4.10 show the rocking curves for the four samples using (224) lattice planes. As indicated in these figures, the peaks are broader than those collected from the (004) reflection. In addition, a peak separation between substrate and epilayer is evident. This remarkable peak separation in the (224) asymmetric reflection can be attributed to distortions in both the perpendicular and parallel directions to the sample surface. The data presented thus far is

not adequate for making a comparison of the crystal quality among the four samples. Also, the cause of the peak broadening cannot be determined from this data.

To solve these issues, rocking curves using the triple axis mode (analyzer crystal) were collected. Using this configuration, it is possible to separate lattice parameter spread versus mosaicity spread in the rocking curve broadening as discussed in Chapter 2. Omega (ω) rocking curves from (004) reflections for the four samples are shown in Figures 4.11 through 4.14. The FWHM of the rocking curves were 20.7, 16.7, 14.4 and 14 arcsec. from the ZnSe epilayers with no treatment, three minute, six minute and nine minute UV-ozone exposure, respectively. All samples except H1 (no UV-ozone treatment) exhibited narrow and symmetric peaks. However, the FWHM values for the remaining three samples are two or three times larger than that of the substrate (7.74 arcsec., see Fig. 3.9) This ω rocking curve broadening is due to the existence of mosaic blocks in the epilayer. In the case of sample H1 (Figure 4.11), the rocking curve has a shoulder on the left side of the peak which is direct evidence of more severe mosaicity spread in the epilayer. The FWHM of the symmetric rocking curves versus UV-ozone exposure duration is shown in Figure 4.19. The sample without UV-ozone treatment, H1, showed the largest FWHM values, whereas the six minute treated sample and nine minute treated sample possessed nearly identical FWHM values of about 14 arcsec.

On the other hand, $\omega/2\theta$ rocking curves recorded from the four samples exhibited two separate individual peaks (Figures 4.15-4.18). It seems that the intense, narrow peaks are mainly from the substrates and the less intense, wider peaks are mainly from the epilayers. This peak separation is primarily due to lattice parameter spread. Since the

samples are homoepitaxial, the angular separation between two peaks is not because of lattice mismatch but because of strain and defects in epilayers. The FWHMs and angular separation between these two peaks for the four samples are listed in Table 4.2.

Table 4.2 FWHM values of $\omega/2\theta$ rocking curves obtained using the analyzer crystal. Peak separations are also listed. The symmetric (004) reflection plane was used.

Sample ID	FWHM of Substrate (arcsec.)	FWHM of Epilayer (arcsec.)	Peak Separation (arcsec.)	Remark
H1	16.2	42.5	50.5	No UV-ozone
H2	17.6	37.8	56.7	3 min. UV-ozone
H3	14.0	33.3	49.0	6 min. UV-ozone
H4	17.1	39.6	56.7	9 min. UV-ozone

As can be seen in Table 4.2, sample H3, which was exposed for 6 minutes to the UV-ozone environment, exhibited the smallest FWHM values and peak separation. Compared with the ω rocking curve broadening, the $\omega/2\theta$ rocking curve broadening is more severe.

Asymmetric reflections using the analyzer crystal were recorded from the (224) lattice planes and are shown in Figures 4.21 to 4.28. FWHM values for both ω and $\omega/2\theta$ scan axes are summarized in Table 4.3. In the case of the ω scan, all four rocking curves (Figures 4.21-4.24) showed symmetric shapes. However, the $\omega/2\theta$ rocking curves exhibited asymmetric peak shapes. Specifically, in the case of samples H1 and H2, large

shoulders were observed at the left side of the peaks. This asymmetry of the peaks can be attributed to defects in the epilayers such as stacking faults [79]. The FWHM of the asymmetric ω and $\omega/2\theta$ rocking curves versus UV-ozone exposure duration are shown in Figure 4.29.

Table 4.3 FWHM values of both ω and $\omega/2\theta$ rocking curves obtained using the analyzer crystal. Asymmetric (224) reflection plane was used.

Sample ID	FWHM of ω rocking curve (arcsec.)	FWHM of $\omega/2\theta$ rocking curve (arcsec.)	Remark
H1	25.2	49.5	No UV-ozone
H2	21.7	29.7	3 min. UV-ozone
H3	22.0	18.9	6 min. UV-ozone
H4	19.0	20.2	9 min. UV-ozone

As indicated in this figure, the FWHM values for the ω rocking curves change only slightly within the four sample set. Sample H1 had the largest value of 25.2 arcsec. and the smallest value, 19 arcsec., was exhibited from sample H4. On the other hand, the FWHM values for the $\omega/2\theta$ rocking curves exhibited were significantly different. Sample H1 possessed the largest value of 49.5 arcsec. whereas sample H3 showed the smallest value of 18.9 arcsec. Samples H1 and H2 exhibited large shoulders. Sample H3 showed the smallest shoulder.

Based on the above results, it can be concluded that the rocking curve broadening observed in the receiving slit mode was due to both a lattice parameter change (strain)

caused by defects and mosaicity in the homoepitaxial epilayers. As the surface roughness decreased, the rocking broadening was also reduced. In other words, both mosaicity and lattice parameter spreads were reduced as the substrate surface roughness decreased.

Photoluminescence Analysis

Low-temperature PL spectra were recorded from samples H1, H2, H3 and H4; these spectra are presented in Figures 4.30, 4.31, 4.32 and 4.33, respectively. A reference sample was measured simultaneously with the samples in order to compare results taken at different times and to determine the condition of the instrument.

The spectra are all indicative of high quality films although the specific *ex vacuo* UV-ozone treatment appears to have a significant impact on the resultant PL characteristics. Figures 4.30(a) and (b) show the PL spectra at 23K recorded from sample H1 (no *ex-situ* substrate treatment). Strong, sharp free exciton, E_X , and neutral donor-bound exciton, I_2 , emissions were observed at 2.803 eV and 2.798 eV, respectively. The intensities for those two emissions were almost identical. A sharp ionized donor-bound exciton (I_3) emission was also found at 2.7966 eV. A small but sharp acceptor bound exciton peak at 2.7925 eV (I^Y_1) was observed. The I_V transition at around 2.777 eV was identified and this transition is believed to be associated with a recombination at some localized intrinsic defect complex [80]. A relatively small so-called Y emission and its phonon replica were identified at 2.605 eV and 2.5737 eV, respectively. It is known that this Y-line emission is directly related to the threading dislocations in the material [81-85]. Dean et al. [85] observed Y emission in metal-organic chemical vapor deposition

(MOCVD) grown heteroepitaxial ZnSe/GaAs and proposed a model involving electron-hole recombination at dislocations. Shahzad et al. [81] also found that the Y emission at ~ 2.6 eV was directly related to structural defects such as threading dislocations using both PL and TEM data.

Figures 4.31(a) and (b) show the PL spectra at 23K recorded from sample H2 (three minute UV-ozone exposure) which illustrates similar PL characteristics to those of sample H1. However, in the case of sample H2, the intensity of the Y peak at 2.605 eV was much stronger than in the case of sample H1. Therefore, it is expected that the three minute UV-ozone treated sample may contain a larger density of structural defects. It is note worthy that there appears a doublet structure (one peak at 2.6105 eV and the other peak at 2.6050 eV) of the Y emission, the peaks being separated from each other by 5.5 meV. In 1985, Taguchi et al. [86] found this doublet structure of the Y emission while they were investigating the PL properties of ZnSe single crystals. They investigated the temperature dependence of the doublet structure and concluded that the doublet originated from the same center and that the higher energy peak (here at 2.6105 eV) might correspond to the excited state of the Y center. This excitation energy was estimated to be about 5.5 meV.

The six minute UV-ozone treated sample exhibited the best PL spectra based on the relative intensity of the free-exciton, E_x , and the relative intensity of the Y emission. The integrated intensities of the E_x and Y emissions were measured for each of the four samples and the ratios of these intensities are plotted in Figure 4.34 as a function of the UV-ozone exposure time prior to growth. The data is normalized to the Y/E_x ratio of

sample H3. As can be seen from the figure, the six minute treated sample showed the lowest Y/E_x ratio. In other words, this sample (H3) appears to have the lowest defect concentration. Actually, this trend follows the surface roughness trend shown in Figure 4.1 except for sample H4. As the surface roughness of the substrate decreased the defect density also decreased based on the PL analysis. The deviation of sample H4 from the trend set by the other three samples may be attributed to a residual oxide on the substrate surface of H4 which may not have been removed in spite of the long exposure time to the hydrogen flux. Another possible explanation is that the long exposure to the hydrogen flux may have caused local roughening at the substrate surface.

Based on the above data, a 6 minute UV-ozone treatment was selected for all future growths in this study.

Summary

We have found that an *in-situ* combined thermal/H-atom treatment for the cleaning of ZnSe substrates is superior to the conventional thermal method in that the combined thermal/H-atom method allowed oxide desorption at a lower temperature (300 °C compared with 500 °C) and resulted in a smoother ZnSe surface as evidenced by the RHEED patterns observed from the cleaned surfaces.

It was possible to modify the ZnSe substrate surface roughness by *ex-situ* UV-ozone exposure treatment. The effects of substrate surface roughness on the quality of MBE-grown ZnSe homoepitaxial layers were examined and it was found that a direct relationship exists between epilayer quality and the substrate surface morphology. Based

on the HRXRD and PL results, a six minute UV-ozone treatment provided the best homoepitaxial layer quality. Both mosaicity and strain were responsible for the rocking curve broadening. The low temperature PL results were in agreement with HRXRD results. In the case of the nine minute treated sample, the epilayer quality was deteriorated due to the problem involved in removing the thicker oxide layer.

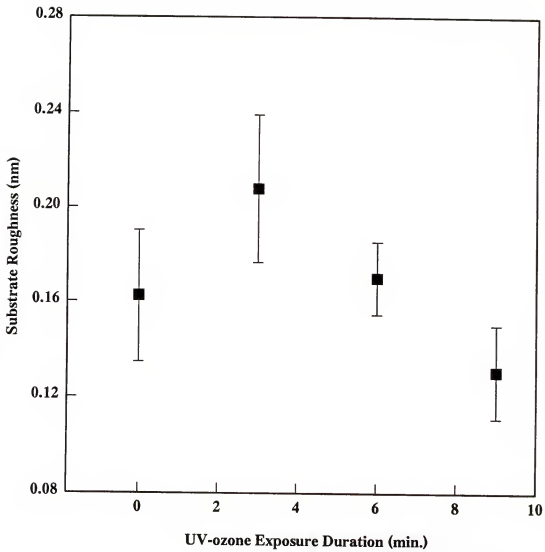


Figure 4.1 UV-ozone exposure duration dependent substrate surface roughness.

[110] azimuth



(a) ZnSe substrate pattern
observed at 300°C

[110] azimuth



(b) ZnSe substrate pattern
observed at 300°C



(c) ZnSe epilayer pattern
observed at 300°C



(d) ZnSe epilayer pattern
observed at 300°C

Figure 4.2 Reflection high energy electron diffraction patterns recorded in two orthogonal azimuths from a H-atom treated ZnSe wafer [(a) and (b)] and a ZnSe homoepitaxial layer [(c) and (d)].

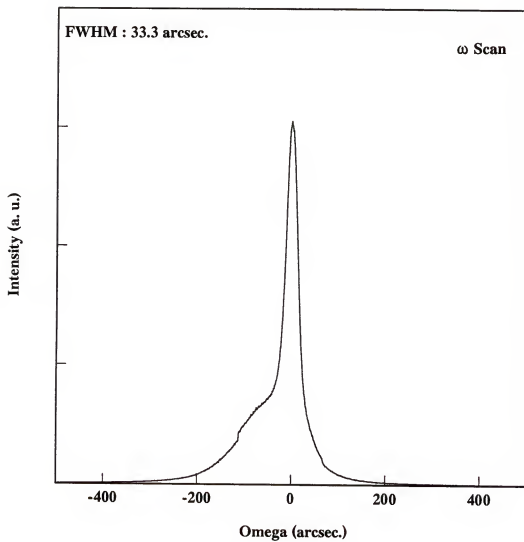


Figure 4.3 X-ray rocking curve of (004) reflection obtained from H1 (No substrate UV-ozone treatment).

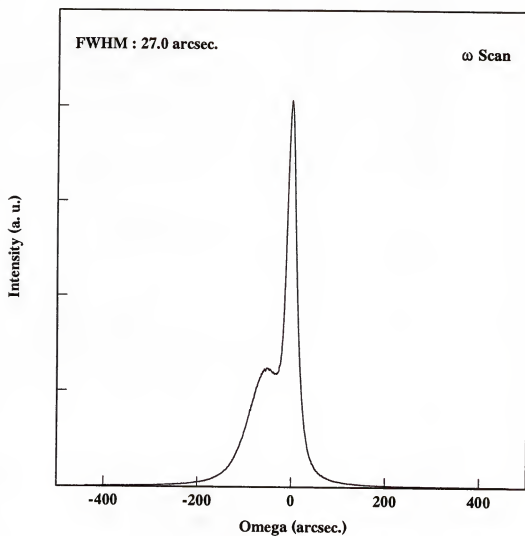


Figure 4.4 X-ray rocking curve of (004) reflection obtained from H2 (3min. substrate UV-ozone).

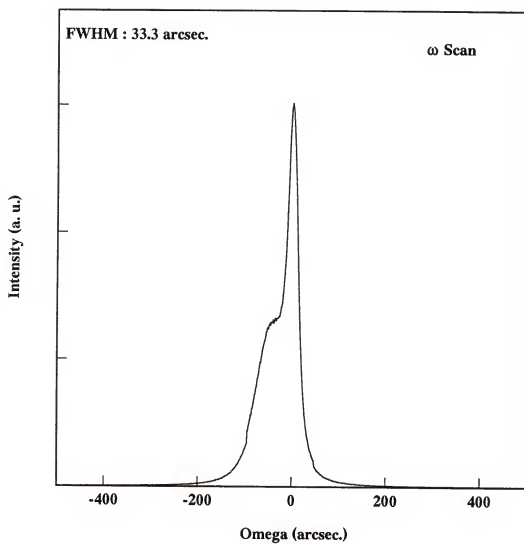


Figure 4.5 X-ray rocking curve of (004) reflection obtained from H3 (6 min. substrate UV-ozone).

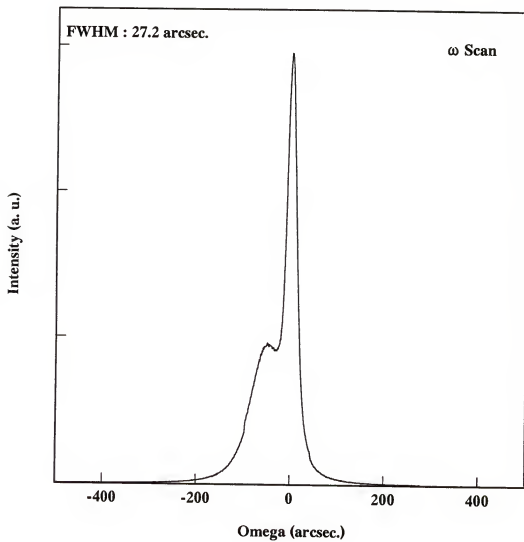


Figure 4.6 X-ray rocking curve of (004) reflection obtained from H4 (9 min. substrate UV-ozone).

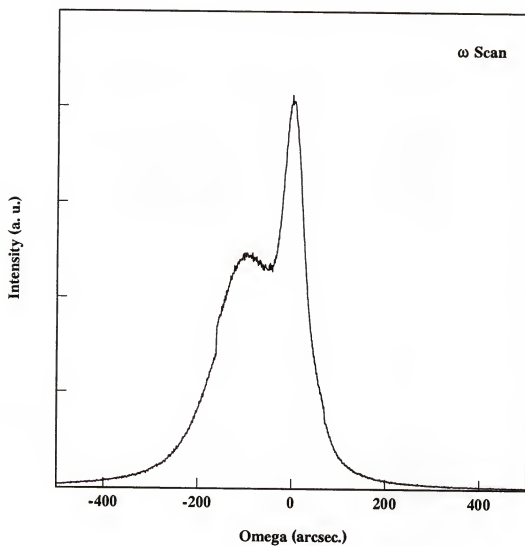


Figure 4.7 X-ray rocking curve of (224) reflection obtained from H1 (No substrate UV-ozone treatment).

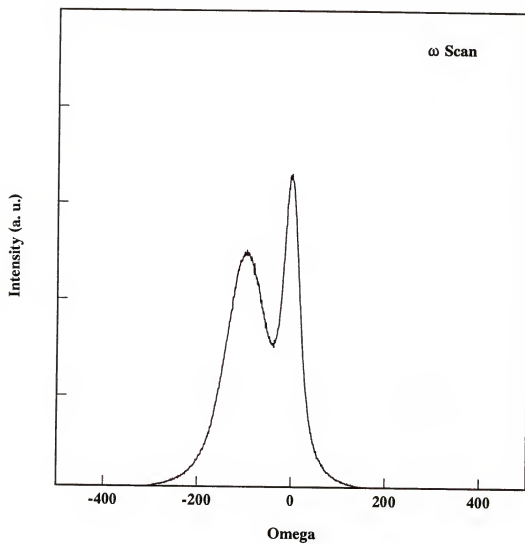


Figure 4.8 X-ray rocking curve of (224) reflection obtained from H2 (3min. substrate UV-ozone).

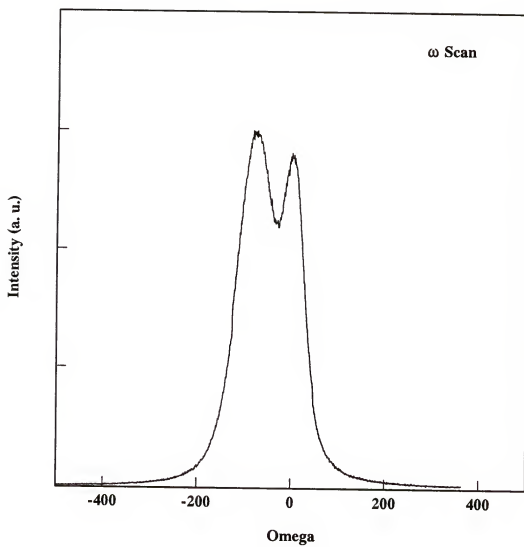


Figure 4.9 X-ray rocking curve of (224) reflection obtained from H3 (6 min. substrate UV-ozone).

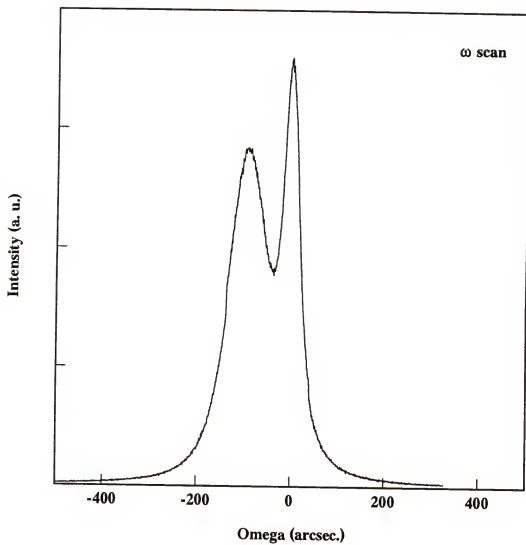


Figure 4.10 X-ray rocking curve of (224) reflection obtained from H4 (9 min. substrate UV-ozone).

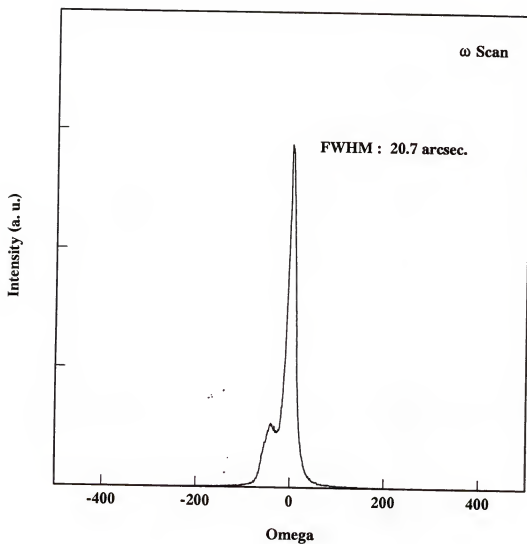


Figure 4.11 X-ray rocking curve of (004) reflection obtained from H1 (No substrate UV-ozone treatment) using nalyzer crystal.

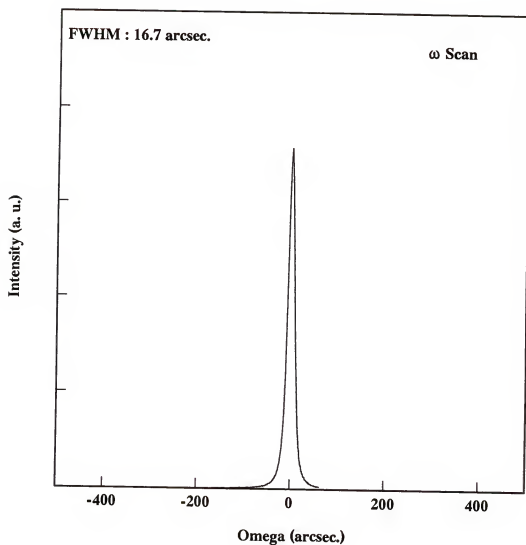


Figure 4.12 X-ray rocking curve of (004) reflection obtained from H₂ (3min. substrate UV-ozone) using analyzer crystal.

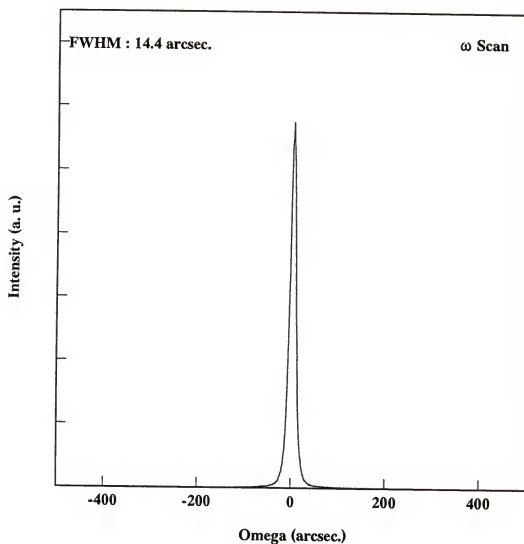


Figure 4.13 X-ray rocking curve of (004) reflection obtained from H3 (6 min. substrate UV-ozone) using analyzer crystal.

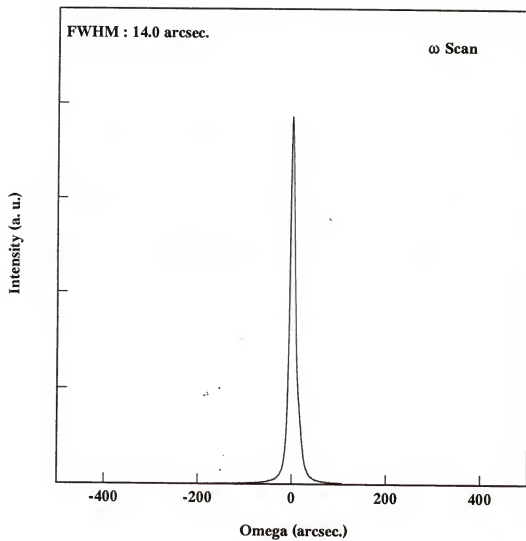


Figure 4.14 X-ray rocking curve of (004) reflection obtained from H4 (9 min. substrate UV-ozone) using analyzer crystal.

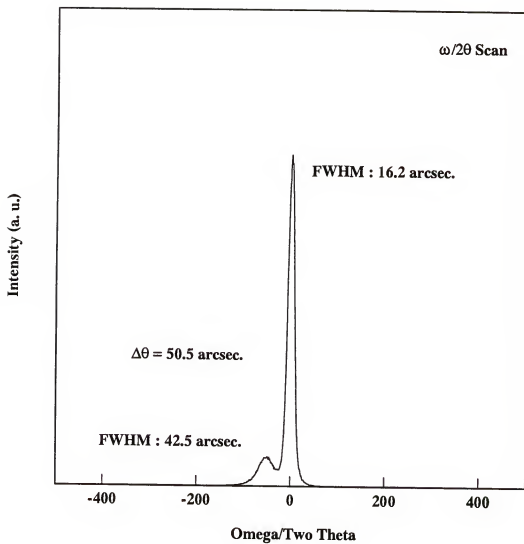


Figure 4.15 X-ray rocking curve of (004) reflection obtained from H1 (No substrate UV-ozone treatment) using analyzer crystal.

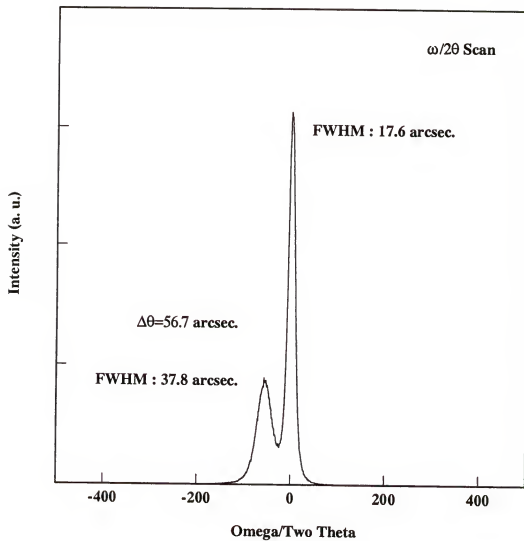


Figure 4.16 X-ray rocking curve of (004) reflection obtained from H2 (3min. substrate UV-ozone) using analyzer crystal.

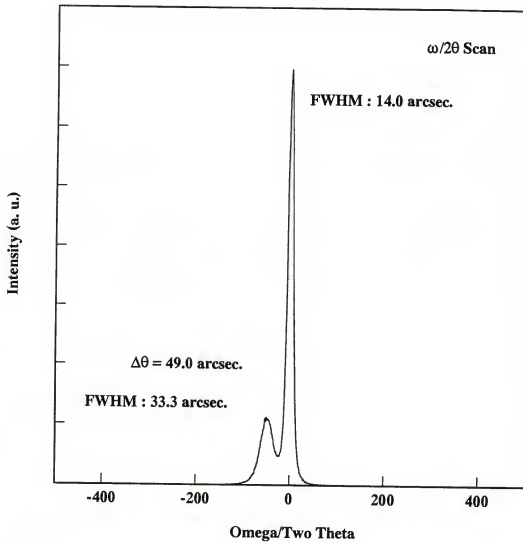


Figure 4.17 X-ray rocking curve of (004) reflection obtained from H3 (6 min. substrate UV-ozone) using analyzer crystal.

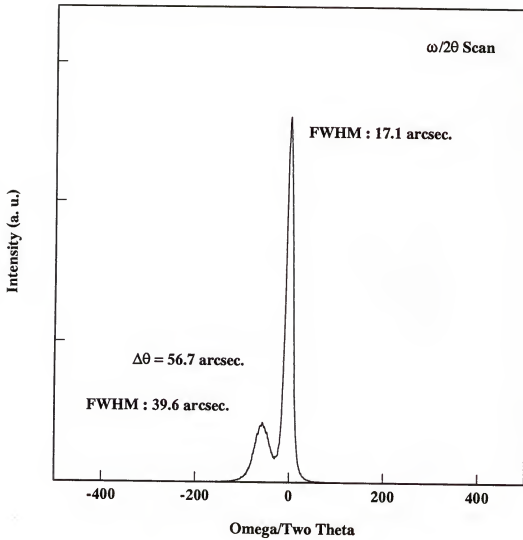


Figure 4.18 X-ray rocking curve of (004) reflection obtained from H4 (9 min. substrate UV-ozone) using analyzer crystal.

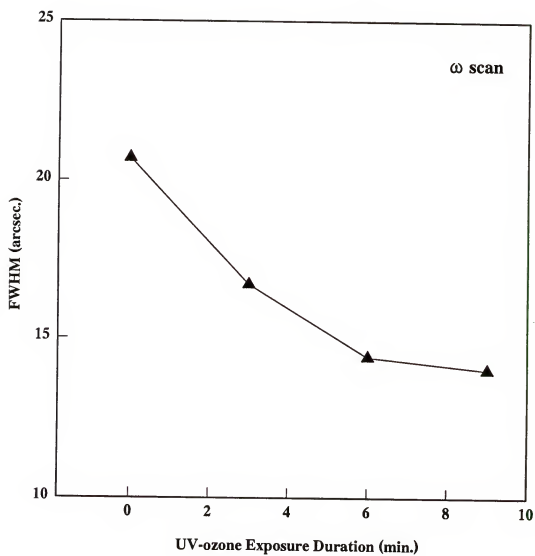


Figure 4.19 Epilayer FWHM values as a function of substrate UV-ozone exposure time. (004) HRXRD was conducted using analyzer crystal.

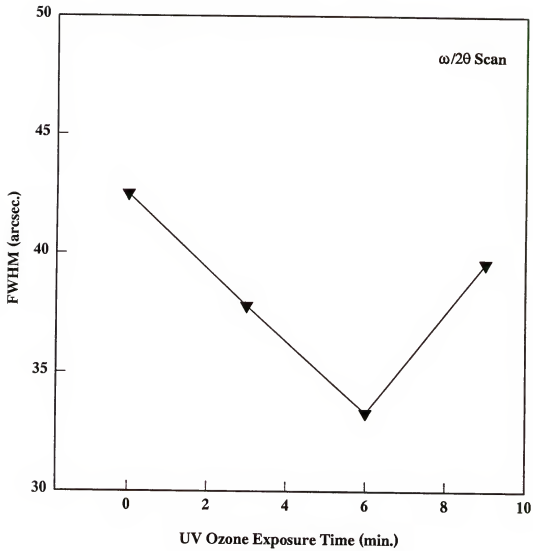


Figure 4.20 Epilayer FWHM values as a function of substrate UV-ozone exposure time. (004) HRXRD was conducted using analyzer crystal.

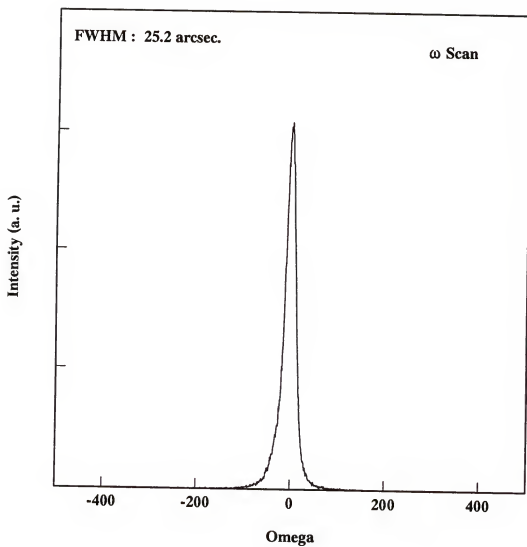


Figure 4.21 X-ray rocking curve of (224) reflection obtained from H1 (No substrate UV-ozone treatment) using analyzer crystal.

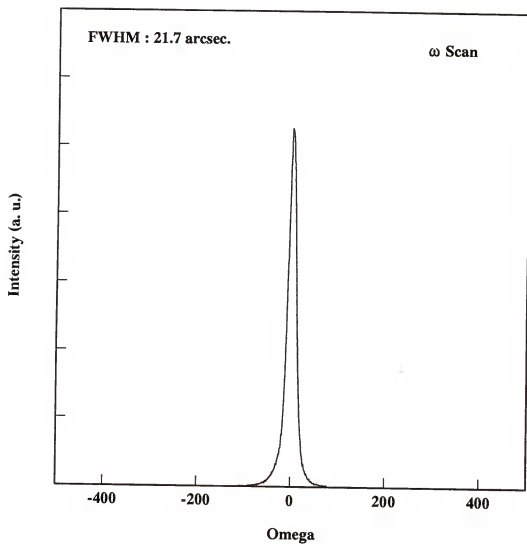


Figure 4.22 X-ray rocking curve of (224) reflection obtained from H2 (3min. substrate UV-ozone) using analyzer crystal.

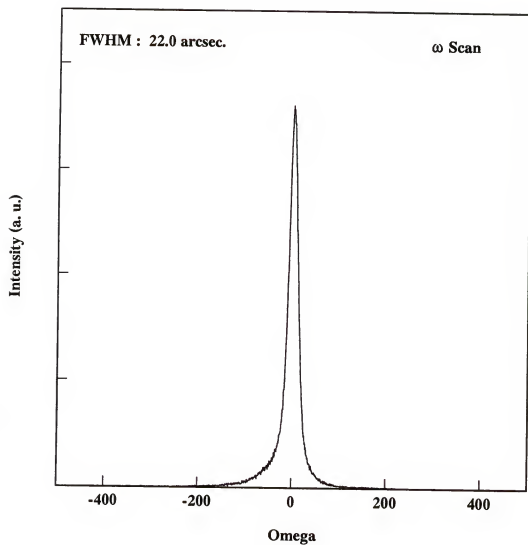


Figure 4.23 X-ray rocking curve of (224) reflection obtained from H3 (6 min. substrate UV-ozone) using analyzer crystal.

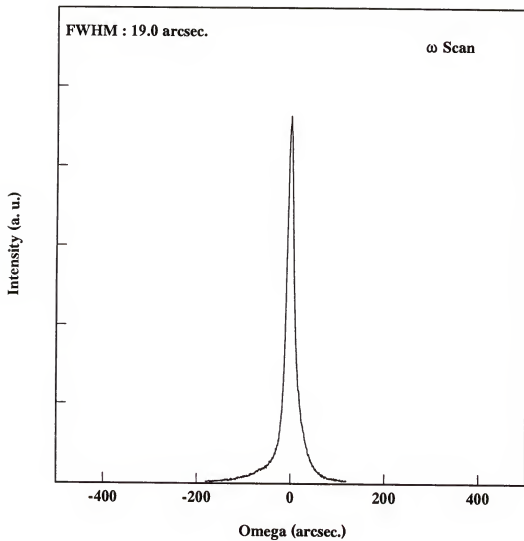


Figure 4.24 X-ray rocking curve of (224) reflection obtained from H4 (9 min. substrate UV-ozone) using analyzer crystal.

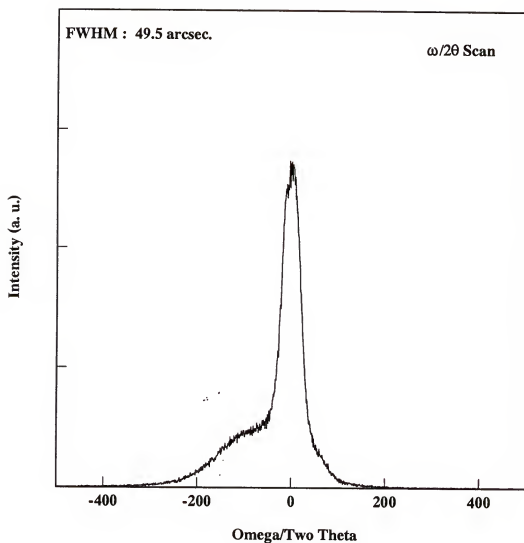


Figure 4.25 X-ray rocking curve of (224) reflection obtained from H1(No substrate UV-ozone treatment) using analyzer crystal.

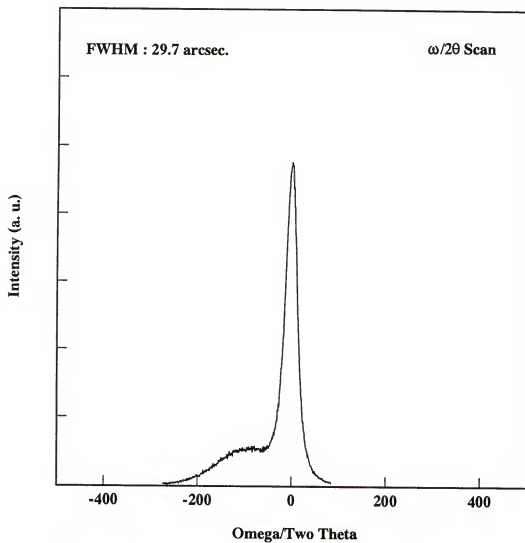


Figure 4.26 X-ray rocking curve of (224) reflection obtained from H2 (3min. substrate UV-ozone) using analyzer crystal.

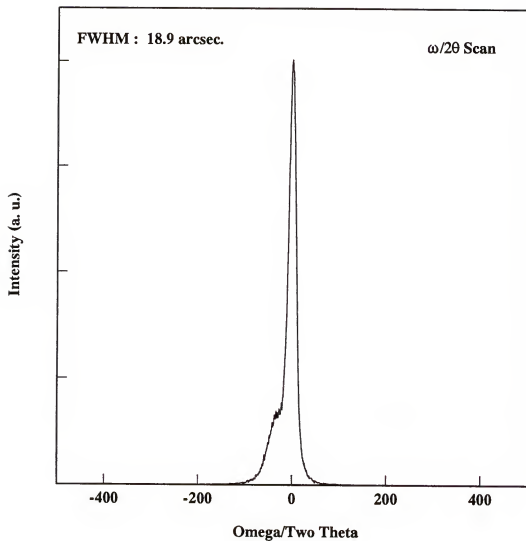


Figure 4.27 X-ray rocking curve of (224) reflection obtained from H3 (6 min. substrate UV-ozone) using analyzer crystal.

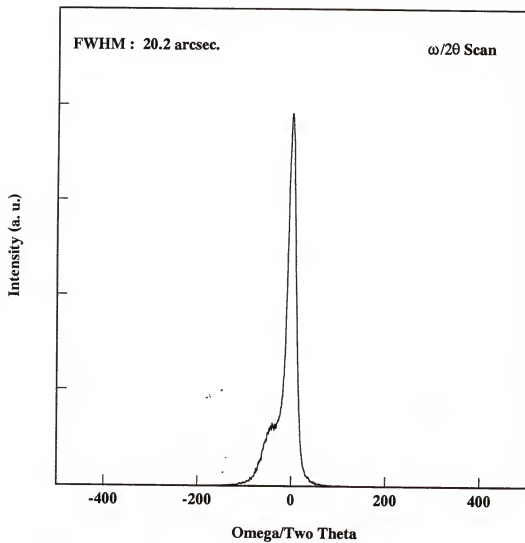


Figure 4.28 X-ray rocking curve of (224) reflection obtained from H4 (9 min. substrate UV-ozone) using analyzer crystal.

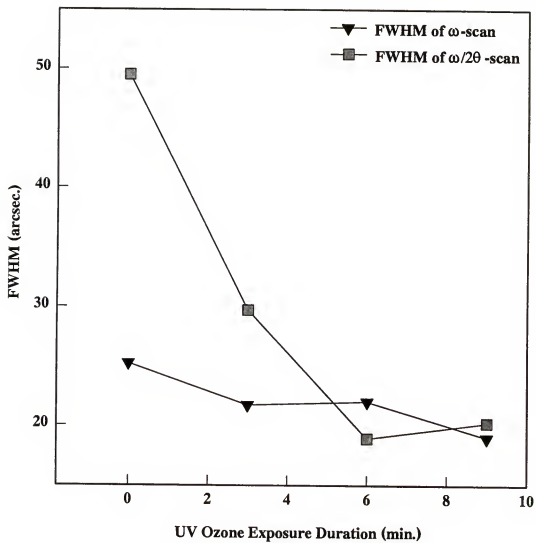


Figure 4.29 Epilayer FWHM values as a function of substrate UV-ozone exposure time. (224) HRXRD was conducted using analyzer crystal

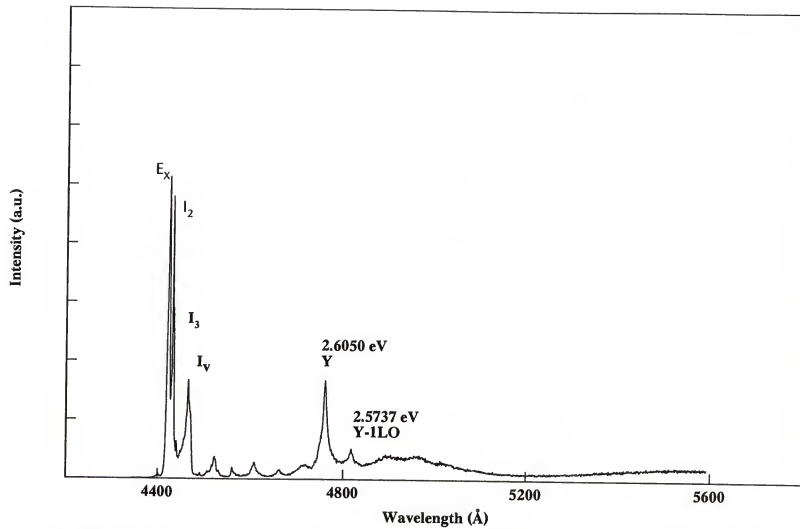


Figure 4.30(a) Low-temperature (23K) PL spectrum recorded from H1 (No substrate UV-ozone treatment).

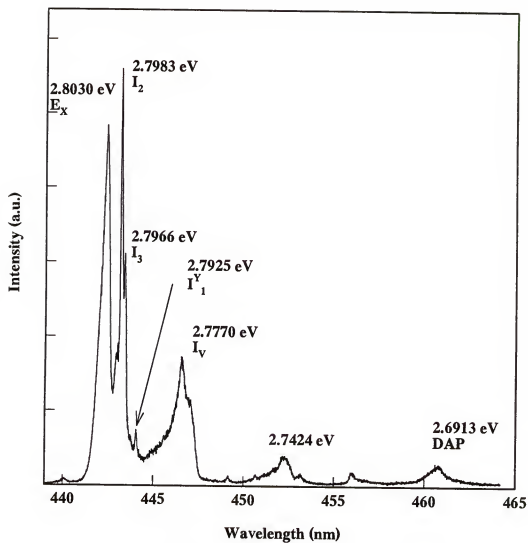


Figure 4.30(b) Low-temperature (23K) PL spectrum recorded from H1 (No substrate UV-ozone treatment). (High resolution)

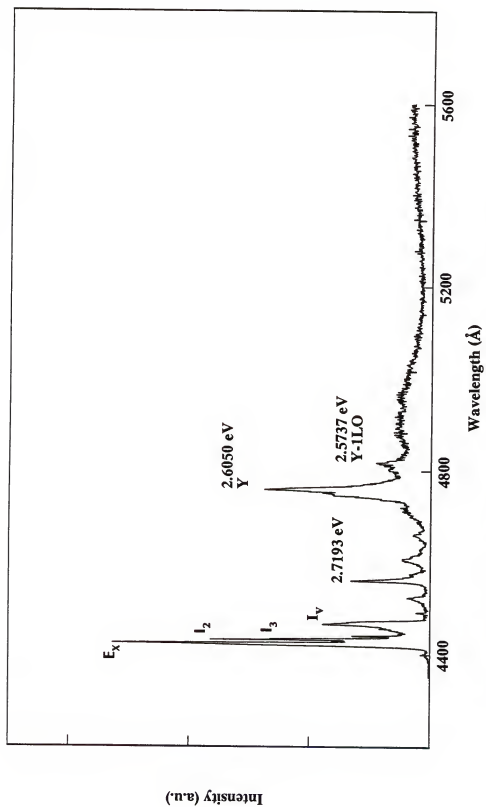


Figure 4.31(a) Low-temperature (23K) PL spectrum recorded from H2 (3 min. substrate UV-ozone)
(Low resolution)

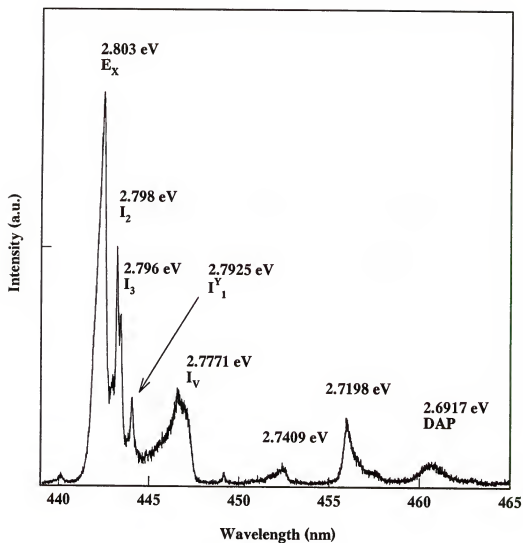


Figure 4.31(b) Low-temperature (23K) PL spectrum recorded from H2 (3 min. substrate UV-ozone). (High resolution)

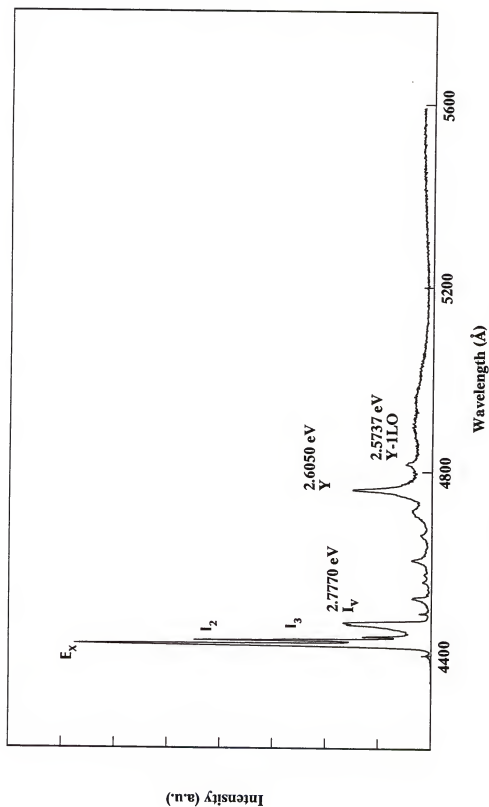


Figure 4.32(a) Low-temperature (23K) PL spectrum recorded from H3 (6 min, substrate UV-ozone).
(Low resolution)

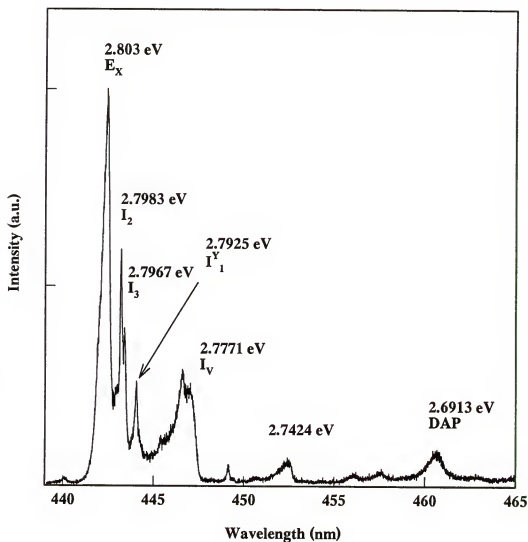


Figure 4.32(b) Low-temperature (23K) PL spectrum recorded from H3 (6 min. substrate UV-ozone). (High resolution)

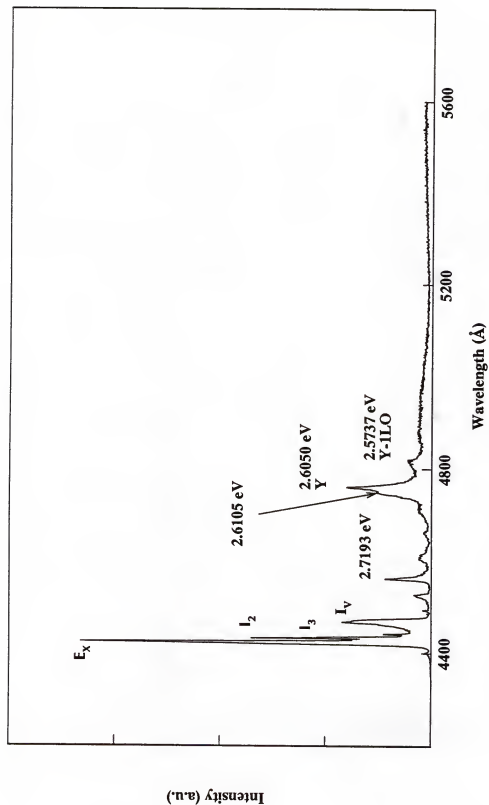


Figure 4.33(a) Low-temperature (23K) PL spectrum recorded from H4 (9 min. substrate UV-ozone). (Low resolution)

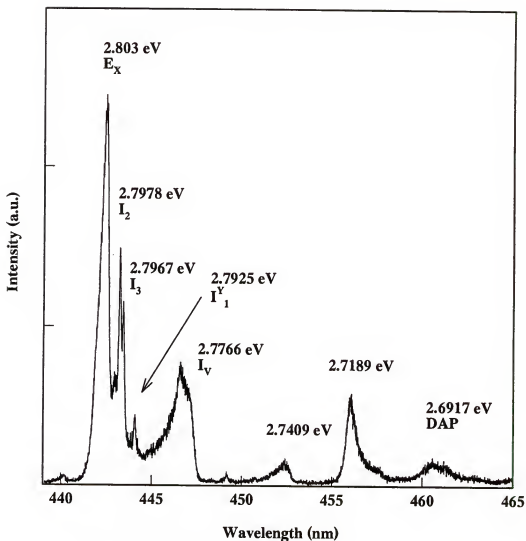


Figure 4.33(b) Low-temperature (23K) PL spectrum recorded from H4(9 min. substrate UV-ozone). (High resolution)

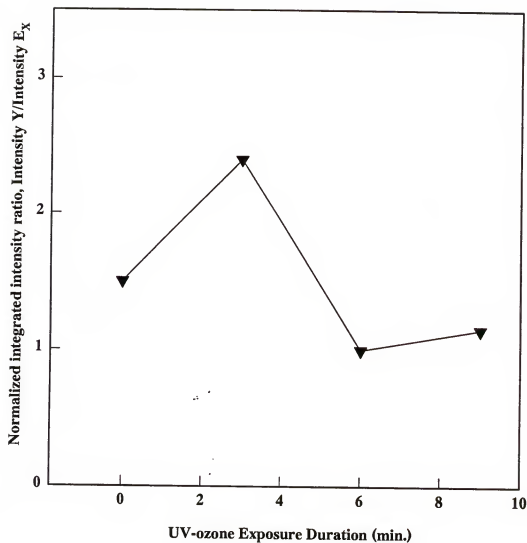


Figure 4.34 Intensity ratio of Y and E_x emissions from low-temperature PL recorded from epilayers grown on substrates having various UV-ozone exposure times.

CHAPTER 5

INVESTIGATION OF A NOVEL ZnSe GROWTH MODE

Introduction

As reviewed in Chapter 1, migration enhanced epitaxy (MEE) has been explored as a growth mode for GaAs as well as ZnSe. In MEE only one shutter is open at any one time and a variety of "shutter open" durations have been investigated for GaAs/GaAs and ZnSe/GaAs growth [53, 54, 61, 87, 88]. In the case of ZnSe growth, "shutter open" or "exposure times" can be large since, for ZnSe, MEE is a self-limiting growth process [59]. The various "shutter open" duration times that have been reported in the literature are summarized in Table 5.1. Also, presented in Table 5.1 are the "delay times" that the various research groups have employed in their work. The "delay time" is the time that is allowed to elapse between closing one shutter and opening the other shutter (for binary compound growth). As can be seen from the table, three different delay times have been reported in the literature for ZnSe MEE growth, namely 0.3 second, 1 second and 6 seconds. In all three of these cases, however, no explanation is offered concerning the choice of delay time.

In this work, we have performed a systematic study concerning the influence of delay time on the quality of ZnSe homoepitaxial layers. As will be described below, our experimental observations suggest that surface relaxation processes occur during the

delay time period as a function of time, particularly in the case of Se surfaces, and, consequently, we have coined the phrase “Surface Relaxation Controlled Epitaxy” (SRCE) to describe our novel growth mode.

Table 5.1 Shutter open durations for the constituent elements and delay times found in the literature for MEE growth of GaAs and ZnSe.

Reference	Ga or Zn shutter open duration (sec.)	As or Se shutter open duration (sec.)	Delay time (sec.)	Material system
[89]	1.1	1.1	None	GaAs/GaAs
[90]	15	15	None	ZnSe/GaAs
[59]	3	4	None	ZnSe/GaAs
[53]	1	3	5	GaAs/GaAs
[87]	0.5	0.5	2	GaAs/GaAs
[62]	10	10	None	ZnSe/GaAs
[91]	7	7	1	ZnSe/GaAs
[54]	2.5	2.5	0.3	ZnSe/GaAs
[61]	3	3	6	ZnSe/GaAs

Growth Procedures

ZnSe substrates were prepared using the optimized *ex-situ* and *in-situ* procedures described previously in this dissertation.

Following *in-situ* wafer cleaning, the ZnSe substrates were exposed to a Se flux for about 2 minutes during which time a Se-stabilized surface developed as evidenced by the observation of a developing (2x1) RHEED pattern.

Thereafter, the substrate was alternately exposed to Zn and Se, in each case the “shutter open” or exposure time was the same, namely 30 seconds. The delay time, however, the time allowed to elapse between closing the Zn shutter and opening the Se shutter, or vice-versa, was systematically varied from run-to-run over the range, 0 to 60 seconds.

Also, in all of the cases to be reported here, this growth mode was in effect for 10 cycles (10 Zn exposures and 10 Se exposures) beyond which conventional MBE growth was performed (both Zn and Se shutters permanently open) until 2 μm of ZnSe had been deposited.

Table 5.2 summarizes the shutter open times and the Zn and Se surface relaxation times (or delay times) employed in this study. The ZnSe homoepitaxial layers grown using the “Surface Relaxation Controlled Epitaxy” (SRCE) growth mode at the initial stages of the growth were characterized by a number of techniques including low-temperature PL, HRXRD, TEM and etch-pit density (EPD) measurements and the results obtained are presented below.

Table 5.2 Shutter open durations and Zn and Se surface relaxation times employed.

Sample ID	Zn shutter open duration (sec.)	Se shutter open duration (sec.)	Zn and Se surface relaxation time (sec.)
H8	30	30	0
H9	30	30	1
H10	30	30	5
H11	30	30	10
H12	30	30	30
H13	30	30	40
H14	30	30	60

Characterization Results

Low temperature PL analysis

Low-temperature PL spectra were recorded from samples H8 to H14 (see Table 5.2) and these spectra are presented in Figures 5.1-5.7, respectively. Spectral characteristics for all samples (H8-H14) were almost identical except for the intensity variations occurring in the Y emissions. Table 5.3 shows the normalized integrated intensity ratio (intensity Y/intensity E_X) versus relaxation time. To obtain integrated intensities for E_X and Y, the area under the E_X peak and the area under the Y peak were integrated in the ranges of 440.5 nm to 442.9 nm and 472.8 nm to 479.2 nm, respectively.

Then, integrated intensity of Y/integrated intensity of E_x ratios were calculated and normalized to the ratio for sample H12. These results are plotted in Figure 5.8.

Table 5.3. Normalized integrated intensity of Y/integrated intensity of E_x ratios for each relaxation time.

Sample ID	Relaxation Time (Sec.)	Normalized integrated intensity of Y/ integrated intensity of E_x
H8	0	3.78
H9	1	2.58
H10	5	2.94
H11	10	2.36
H12	30	1.0
H13	40	1.63
H14	60	4.46

As can be seen in Figure 5.8, the sample H12 which was grown using the 30 second relaxation time exhibited the lowest Y/ E_x ratio. On the other hand, the sample grown using a 60 second relaxation time (H14) exhibited the highest ratio. Since the Y emission is directly related to threading dislocations, it can be concluded that the 30 second relaxation time appears to be optimum at least from the PL data.

HRXRD Analysis

HRXRD analysis was conducted to determine the effect of relaxation time on the epilayer quality. X-ray rocking curves were recorded using both the five- and seven crystal configurations as described in Chapter 4. Also, as indicated in Chapter 4, rocking

curves recorded using the five-crystal configuration did not provide enough information to assess epilayer quality mainly due to poor resolution. The analyzer crystal in the seven-crystal configuration, however, improves the resolution of the x-ray diffractometer. Rocking curves recorded using this configuration will be primarily used. Three representative samples (samples H8, H12 and H14) were selected to record the rocking curves from the (004) and (224) reflections.

Omega (ω) rocking curves from the (004) reflections for the three samples are shown in Figures 5.9-5.11. The FWHM of the curves were 13.5, 10.8 and 16.2 arcsec. from the ZnSe epilayers with zero, 30 and 60 seconds relaxation times, respectively (Figure 5.12). Sample H12 for which a 30 second relaxation time was employed exhibited the narrowest rocking curve line width. Recalling the FWHM value of the substrate (7.75 arcsec., see Fig. 3.9), there is only a 39% increase in FWHM value for sample H12. Also, recalling the FWHM value of sample H3 (14.4 arcsec., see Fig. 4.13), a sample grown by conventional MBE, a 25 % reduction of ω rocking curve linewidth was achieved. This reduction in ω rocking curve linewidth suggests that the mosaicity in the ZnSe epilayer was reduced and, consequently, the structural quality of the epilayer was improved. However, in the case of the $\omega/2\theta$ rocking curve (Figures 5.13-5.15), the differences among these three samples are slight as indicated in Table 5.4. Therefore, the strain in the three samples is similar based on the $\omega/2\theta$ rocking curves, whereas sample H12 exhibited the smallest mosaicity spread in the epilayer in the vertical direction to the substrate.

Table 5.4 FWHM values of the $\omega/2\theta$ rocking curves obtained using the analyzer crystal. The peak separations are also listed. The symmetric (004) reflection plane was used.

Sample ID	FWHM of Substrate (arcsec.)	FWHM of Epilayer (arcsec.)	Peak Separation (arcsec.)	Relaxation time (sec.)
H8	20.7	44.1	52.2	0
H12	19.8	40.5	54.0	30
H14	19.0	42.0	52.2	60

Asymmetric reflections using the analyzer crystal were recorded from the (224) lattice planes and are shown in Figures 5.16 to 5.21. FWHM values for both ω and $\omega/2\theta$ scan axes are summarized in Table 5.5.

Table 5.5 FWHM values of both the ω and the $\omega/2\theta$ rocking curves obtained using analyzer crystal. The asymmetric (224) reflection plane was used.

Sample ID	FWHM of ω rocking curve (arcsec.)	FWHM of $\omega/2\theta$ rocking curve (arcsec.)	Relaxation time (sec.)
H8	21.3	25.2	0
H12	25.0	25.2	30
H14	25.2	25.5	60

As can be seen from the Table 5.5, almost identical FWHM values were obtained in the case of the $\omega/2\theta$ rocking curves. Recalling the FWHM value of substrate (23.4 arcsec., see Fig. 3.12), the broadening of the rocking curves was relatively small, although all three rocking curves exhibited some asymmetry which is indicative of the presence of structural defects such as stacking faults [79]. The omega (ω) rocking curves for samples H8 and H12 possessed almost identical FWHM values (about 25 arcsec.) and exhibited symmetric shapes for both cases. However, in the case of sample H8, a small shoulder was evident although it possessed a smaller FWHM value of 21.3 arcsec.

TEM Analysis

Cross-sectional transmission electron microscopy (XTEM) specimens were prepared and examined for samples H8, H12 and H14 and TEM micrographs are shown in Figures 5.22-5.24, respectively. As the figures indicate, the homointerface is visible intermittently in all three samples. Figure 5.22 shows the interface area between the ZnSe substrate and the epilayer at two different locations for sample H8. Circular-shaped dislocations are present where the homointerface should be based on thickness measurements. The interface is not present between circular-shaped dislocations as indicated in Figure 5.22 (a). Also, as can be seen from Figure 5.22 (a), threading dislocations were initiated at the circular-shaped dislocations. Figure 5.22 (b) shows another location of the homointerface from sample H8. As can be seen from the figure, a dark line exists at the interface which suggests strain at the interface. Threading dislocations were also initiated at the dark line; however, stacking faults are not observed

in this sample. Figure 5.23 (a) and (b) show the XTEM micrographs for sample H12. These figures illustrate similar patterns of dark line interfaces and “no-interfaces” as seen in Figure 5.22, however, circular-shaped dislocation and stacking faults are not seen. Figure 5.24 shows the XTEM micrographs for sample H14. Tangled threading dislocations can be seen in Figure 5.24 (a). Some of these threading dislocations initiate at the interface and some of them propagate up from the substrate. These tangled threading dislocations are also observed in samples H8 and H12; however, the frequency of observation of these regions was less in the case of sample H12. The tangled dislocation regions were most commonly observed in the case of sample H14 and a stacking fault is also observed in this sample as indicated in Figure 5.24 (a). The stacking fault was, however, not initiated at the interface but rather it was initiated at a threading dislocation located in the middle of epilayer.

Although it is extremely difficult to quantify the amount of visible interface in order to compare and assess samples using this technique, it is possible to qualitatively assess these samples. Based on the XTEM observation, it appears that sample H12 contains more “no-interface” regions compared with samples H8 and H14. These observations seem to support the conclusions drawn from the PL data, namely that a 30 second relaxation time appears to be optimum with regard to maximizing crystal quality.

Etch-Pit Density Analysis

To quantitatively assess the defect density, selected samples were sent to the 3M Company for etch-pit density (EPD) analysis. As discussed in Chapter 3, it is known that

each etch-pit corresponds to a stacking fault; therefore, stacking fault density can be directly obtained from the etch-pit density. Samples H8, H11, H12, H13 and H14 received etch-pit analysis and stacking fault densities measured for these samples are listed in Table 5.6. Figure 5.25 shows the relaxation time dependent stacking fault densities. As can be seen from this figure, the lowest stacking fault density of $6 \times 10^4 \text{ cm}^{-2}$ was obtained for the sample grown using a relaxation time of 30 seconds. Sample H8, grown with zero relaxation time, exhibited the highest stacking fault density ($5 \times 10^6 \text{ cm}^{-2}$).

These results are novel as well as exciting and suggest that the density of stacking faults in ZnSe epilayers can be controlled by appropriate control of the growth mode at initial stages of growth.

Table 5.6 Relaxation time dependent stacking fault densities determined by EPD test.

Sample ID	Relaxation time (sec.)	Stacking fault density (cm^{-2})
H8	0	5×10^6
H11	10	2×10^6
H12	30	6×10^4
H13	40	2×10^5
H14	60	5×10^5

A Concept of Surface Relaxation Controlled Epitaxy

Introduction

As suggested by all of the characterization results, sample H12, for which a 30 second relaxation time was employed, exhibited the best structural quality. In particular, low-temperature PL analysis revealed the H12 sample to have the smallest Y emission, suggesting the lowest threading dislocation density. The trend exhibited by the PL data (Figure 5.8) with regard to the relaxation time variation correlates well with the EPD results (Figure 5.25); sample H12 exhibited the lowest stacking fault density of $6 \times 10^4 \text{ cm}^{-2}$. Furthermore, sample H12 exhibited the narrowest ω rocking curve line width of 10.8 arcsec. (Figure 5.12) although the differences among samples (H8, H12 and H14) were slight in the case of the $\omega/2\theta$ rocking curves.

Hence, an optimum Se surface relaxation time of 30 seconds was identified for a substrate temperature of 298 °C which resulted in the lowest stacking fault density and the lowest threading dislocation density. Therefore, it can be concluded that a direct correlation exists between relaxation time and defect evolution.

In this section, details of the novel growth mechanism that we have termed “Surface Relaxation Controlled Epitaxy” (SRCE) will be discussed. First, though, the ZnSe surface structures observed for Zn- and Se-stabilized surfaces as discussed in the literature will be reviewed. This will be followed by a presentation of RHEED observation results pertaining to the Se exposure phase and the Se surface relaxation

phase of our growth mode. Finally, a model for Se-desorption will be suggested based on our experimental and theoretical analyses.

ZnSe Surface Structures

There have been relatively few reports in the literature concerning surface structure of ZnSe. In 1987, Menda et al. [92] reported the kinetic behavior of Zn and Se adatoms on the (001) ZnSe surface. These authors found that a $c(2 \times 2)$ reconstructed surface represented a Zn-stabilized surface while a (2×1) reconstructed surface represented a Se-stabilized surface based on RHEED observations. These authors also measured Se desorption times at different substrate temperatures by observing the transition from a (2×1) to a $c(2 \times 2)$ reconstructed surface after the Se flux was shut off and a typical Arrhenius type behavior was observed. It was found that the activation energy for Se desorption from the surface was 1.02 eV (23.5 kcal/mol). A similar activation energy for Se desorption was obtained by Cornelissen et al. [93] who found that the activation energy for Se desorption was 1.2 eV based on similar RHEED observations.

Yao et al. [94] observed a (2×1) reconstruction for the Se-stabilized surface, while a mixture of (1×2) and $c(2 \times 2)$ surface structures was observed for the Zn-stabilized surface. In addition, these authors monitored the intensity variation of the specular reflection as a function of time during Se desorption from the Se-stabilized surface after the Se shutter was closed and concluded that the activation energy for Se sublimation was 0.66 eV (15.1 kcal/mol). However, it was suggested that the intensity variation of the

specular reflection was not sensitive enough to provide an accurate activation energy determination [93].

Farrell et al. [95] proposed that the Zn-stabilized $c(2 \times 2)$ and the Se-stabilized (2×1) reconstructed structures were due to Zn dimer formation and Se dimer formation, respectively. However, shortly thereafter, these authors [96] investigated the structure and composition of the $c(2 \times 2)$ surface and suggested that this surface was not terminated with Zn dimers, but rather, with a half atomic layer of Zn atoms based on x-ray photoemission (XPS) experiments. On the other hand, these authors suggested that a (2×1) Se-stabilized surface would be a dimerized, fully covered ($\Theta = 1$) surface.

Garcia and Northrup [97, 98] investigated the relative stability of various possible ZnSe(100) surface reconstructions using total energy calculations. They determined and compared the surface energies for various possible reconstruction models as a function of the Zn chemical potential and concluded that a $c(2 \times 2)$ reconstruction with a half-monolayer ($\Theta = 1/2$) coverage of Zn atoms was the most stable in the case of a Zn-stabilized surface, whereas a (2×1) , full monolayer covered ($\Theta = 1$) Se-dimer structure was the most stable for a Se-stabilized surface.

RHEED Observations

RHEED patterns were observed and recorded in this work during Se exposure and during the delay (or relaxation) time following Se exposure prior to Zn exposure. Figures 5.26(a)-(e) show the RHEED patterns recorded in the $[110]$ azimuth during Se

exposure and 12 seconds, 20 seconds, 30 seconds and finally 40 seconds after the Se shutter was closed, respectively. The orthogonal azimuth, $([1\bar{1}0])$, was also examined but showed no higher order diffraction lines. As can be seen from Figure 5.26(a), a half-order diffraction line was identified in the $[110]$ azimuth during Se exposure, indicative of a (2×1) Se-stabilized surface. After the Se shutter was closed, the half-order diffraction lines began to fade out as a function of time. The half-order diffraction lines were only faint after 30 seconds and these lines were not observable 40 seconds after the Se shutter was closed. In addition to the above azimuths, the $[010]$ azimuth was also examined. Figures 5.27(a)-(c) show the RHEED patterns recorded in the $[010]$ azimuth during Se exposure and 28 seconds and 90 seconds after the Se shutter was closed, respectively. A bulk-like diffraction pattern was observed in this azimuth during Se exposure as shown in Figure 5.27(a) and this pattern persisted until approximately 28 seconds after the Se shutter was closed (Figure 5.27(b)). However, beyond this 28 second time frame, half-order diffraction lines began to appear in this azimuth and were fully developed 90 seconds after the Se shutter was initially closed (Figure 5.27(c)). The appearance of the half-order diffraction lines in the $[010]$ azimuth suggests the development of a $c(2\times 2)$ Zn-stabilized surface and is direct evidence of Se desorption. Therefore, it is concluded that in our case for a substrate of $298\text{ }^{\circ}\text{C}$ a (2×1) Se-stabilized surface was observed during Se exposure, then, after the Se shutter was closed, the (2×1) reconstructed surface relaxed to a (1×1) unreconstructed surface in approximately 30 seconds and finally, after approximately an additional 60 seconds, the surface became Zn-stabilized. Our observations suggest that the Se-stabilized surface takes about 30 seconds

to relax to the (1x1) unreconstructed surface at 298 °C. Therefore, a "relaxation time" can be defined as the time required for the (2x1) reconstructed surface to relax to the (1x1) unreconstructed surface. Figure 5.28 summarizes the time line for the Se desorption process for a substrate temperature of 298 °C.

Figures 5.29(a)-(c) show the RHEED patterns recorded in the [010] azimuth during Zn exposure and after the Zn shutter was closed. As can be seen from the figure, half-order diffraction lines were observed during Zn exposure and after the Zn shutter was closed. The other azimuths namely, [110] and $[1\bar{1}0]$, were also examined and only bulk-like patterns were observed during Zn exposure and after the Zn shutter was closed. Therefore, it is concluded that a c(2x2) Zn-stabilized surface was observed during Zn exposure and even after the Zn shutter was closed.

Model for Se Desorption

Based on our RHEED observations, the (2x1) reconstructed Se-dimer structure relaxed to a (1x1) unreconstructed, fully covered Se-monomer structure in about 30 seconds at our growth temperature of 298 °C. Beyond the 30 seconds, it is expected that these monomerized Se atoms begin to be desorbed from the surface. In order to identify activation energies for Se-monomerization and Se-desorption, the times required for the Se-monomerization and Se-desorption were recorded as a function of the substrate temperature. The Se-monomerization time is virtually the same as the "relaxation time" at a given growth temperature and can be defined as the time required for the (2x1) reconstructed surface to relax to the (1x1) unreconstructed surface. Hence, Se-

monomerization times at different substrate temperatures were measured by monitoring the half-order diffraction lines in the [110] azimuth. On the other hand, the Se-desorption times were recorded by monitoring the appearance of half-order diffraction lines in the [010] azimuth at different substrate temperatures. Figure 5.30 shows the typical Arrhenius-type plots that were observed. From the slopes of the best-fit lines, the activation energies were found to be 0.862 eV and 0.36 eV for Se-monomerization and Se-desorption, respectively.

The Se desorption process is, in fact, thermodynamically favorable. The Gibbs free energy change [99] for this Se desorption process can be expressed as follows;

$$\Delta G = -R \cdot T \cdot \ln (p_{eq}/p_o)$$

where ΔG is the Gibbs free energy change, $T = 571.15K$, $R = 8.3144$ joules/degree-mole, p_{eq} is equilibrium vapor pressure of Se or Zn and p_o is initial pressure (in our case, about 1×10^{-8} mbar). The equilibrium vapor pressures for Zn and Se at 298 °C are about 2×10^{-3} mmHg (2.666×10^{-3} mbar) and 2×10^{-1} mmHg (2.666×10^{-1} mbar), respectively [102]. Hence, the Gibbs free energy changes related to desorption for Zn and Se are -59.329 kJ/mol (-0.61 eV/atom) and -81.198 kJ/mol (-0.84 eV/atom), respectively. Consequently, the Zn-stabilized surface is thermodynamically more stable than the Se-stabilized surface. This was also confirmed by Menda et al. [92]. Therefore, the system tries to minimize the total Gibbs free energy by desorption of Se atoms and the Zn-stabilized surface will be finally achieved in the absence of Se exposure. Since the Zn-stabilized $c(2 \times 2)$ reconstruction was found to be stable [97, 98], this surface is not expected to transform to another phase.

During the Se desorption process, an intermediate transition from the Se-stabilized (2x1) reconstructed surface to an unreconstructed (1x1) Se-monomer surface seems to be kinetically more favorable rather than direct desorption of Se₂ gas phase from the Se-stabilized (2x1) reconstructed surface as suggested by Menda et al. [100]. It is found that the Se-Se bond strength is about 3.5 eV/bond (79.5 kcal/mol) compared with the Se-Zn bond strength which is about 1.5 eV/bond (35 kcal/mol) [101]. In order for a dimer of Se to be free, four Zn-Se bonds must be broken (6 eV), whereas only two Zn-Se bonds need to be broken (3 eV) in order for a monomer Se atom to be free. To break a Se-Se bond, only 3.45 eV is required. Therefore, our proposed desorption process is a two-step kinetic process: Step (1) breaking of Se-Se dimer bonds with the surface becoming (1x1) unreconstructed. Step (2) breaking of Zn-Se bonds with the surface becoming Zn-terminated. Since the (1x1) unreconstructed surface should be ideally suited for Zn adsorption, we believe that the optimum time to open the Zn shutter would be after step (1) is completed (apparently ~ 30 seconds for substrate temperature of 298 °C). Figure 5.31 summarizes the Se-desorption model. Application of longer relaxation times is not appropriate since Se desorption will begin to occur (step (2)) and indeed we observed that poorer quality films were grown employing longer relaxation times (sample H13 (40 sec. delay) and sample H14 (60 sec. delay)).

Summary

A systematic study concerning the influence of relaxation time on the quality of ZnSe homoepitaxial layers was performed. Sample H12 which was grown using the 30

second relaxation time exhibited the lowest Y/E_x ratio. Since the Y emission is directly related to threading dislocations, the 30 second relaxation time appears to be optimum at least from the PL data. The trend exhibited by the PL data (Figure 5.8) with regard to relaxation time variation correlates well with the trend shown by the EPD results (Figure 5.25); Sample H12 possesses the lowest stacking fault density of $6 \times 10^4 \text{ cm}^{-2}$. Furthermore, Sample H12 exhibited the narrowest ω rocking curve line width of 10.8 arcsec. (Figure 5.12). Therefore, it was identified that the optimum relaxation time to deposit high quality homoepitaxial ZnSe layers was 30 seconds at 298 °C.

It was found that the Zn-stabilized surface is thermodynamically more stable than the Se-stabilized surface based on the Gibbs free energy calculations. The Gibbs free energy changes related to desorption for Zn and Se are -59.329 kJ/mol (-0.61 eV/atom) and -81.198 kJ/mol (-0.84 eV/atom), respectively. Therefore, the system tries to minimize the total Gibbs free energy by desorption of Se atoms and the Zn-stabilized surface will be finally achieved in the absence of Se exposure. It is proposed that the Se desorption process is a two step kinetic process; step (1) involving Se-Se dimer bond breaking with the surface becoming (1x1) unreconstructed and step (2) breaking of Zn-Se bonds with the surface becoming Zn-stabilized. Based on the above considerations, a new growth mode termed "Surface Relaxation Controlled Epitaxy" was proposed. In this growth mode, the Zn shutter should be opened just after the (2x1) Se-stabilized surface is fully relaxed to a (1x1) unreconstructed surface.

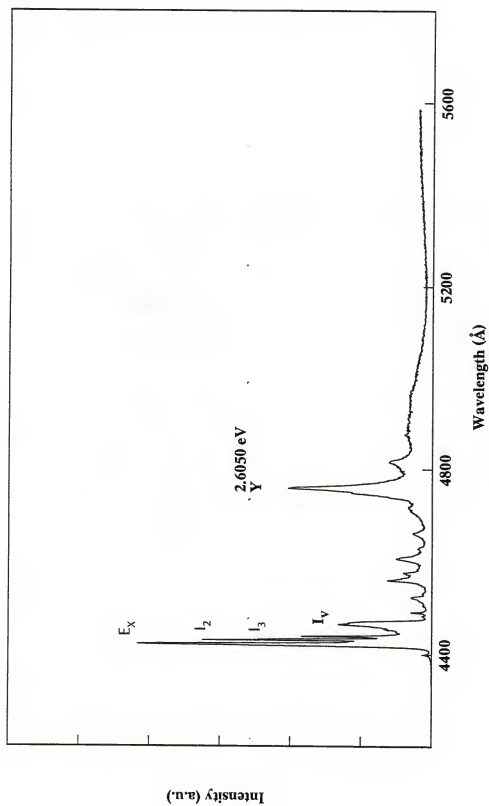


Figure 5.1(a) Low-temperature (23K) PL spectrum recorded from H8 (Low resolution).

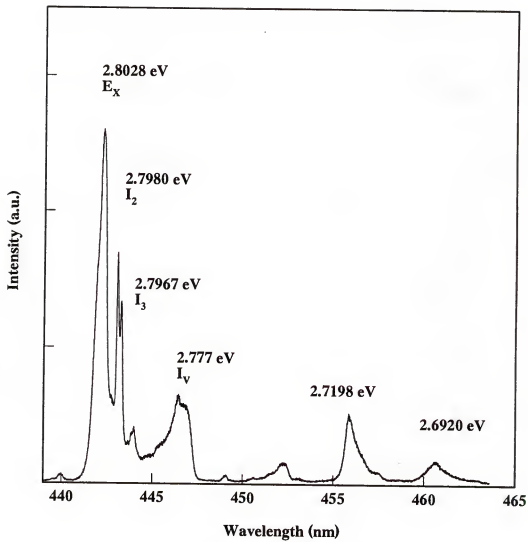


Figure 5.1(b) Low-temperature (23K) PL spectrum recorded from H8.
(High resolution)

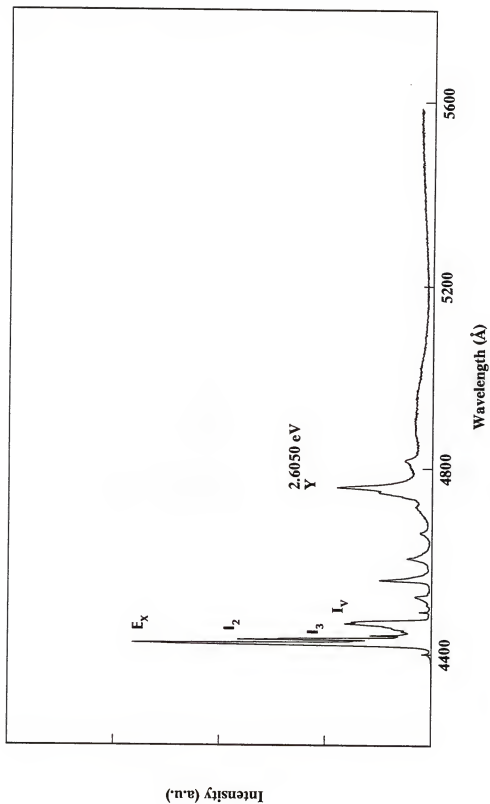


Figure 5.2(a) Low-temperature (23K) PL spectrum recorded from H9 (low resolution).

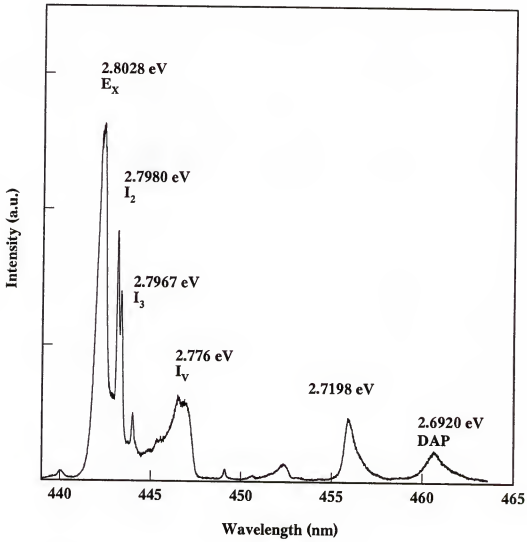


Figure 5.2(b) Low-temperature (23K) PL spectrum recorded from H9. (High resolution)

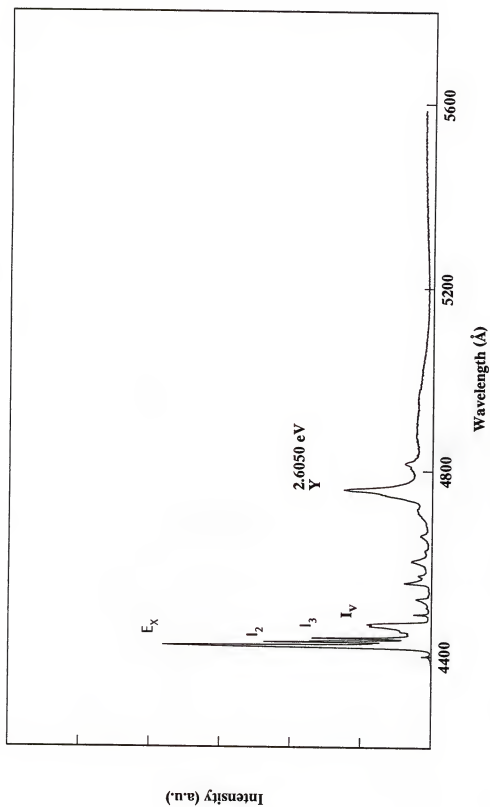


Figure 5.3(a) Low-temperature (23K) PL spectrum recorded from H10 (Low resolution).

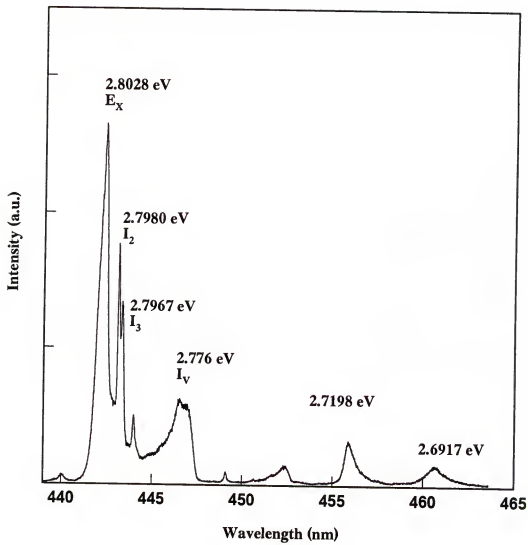


Figure 5.3(b) Low-temperature (23K) PL spectrum recorded from H10. (High resolution)

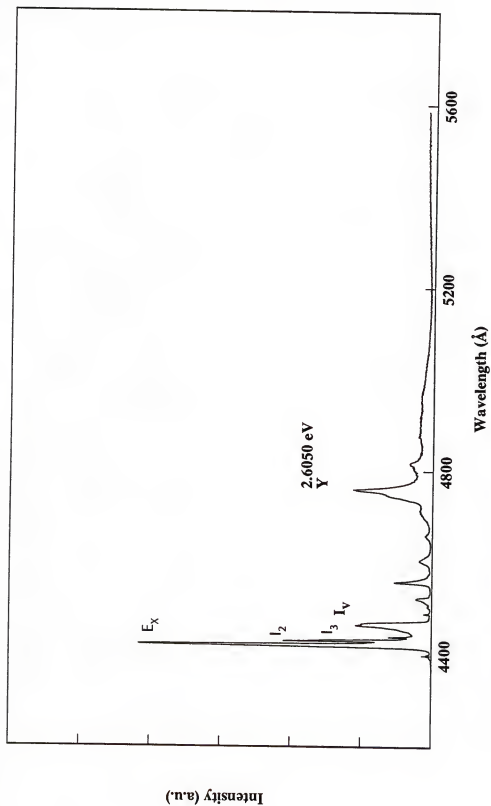


Figure 5.4(a) Low-temperature (23K) PL spectrum recorded from H11 (Low resolution).

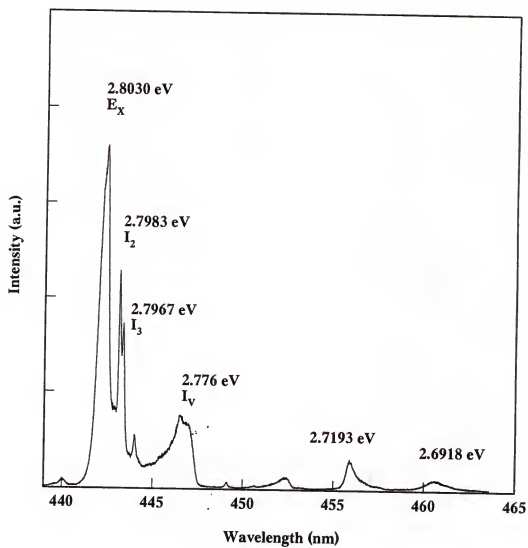


Figure 5.4(b) Low-temperature (23K) PL spectrum recorded from H11.
(High resolution)

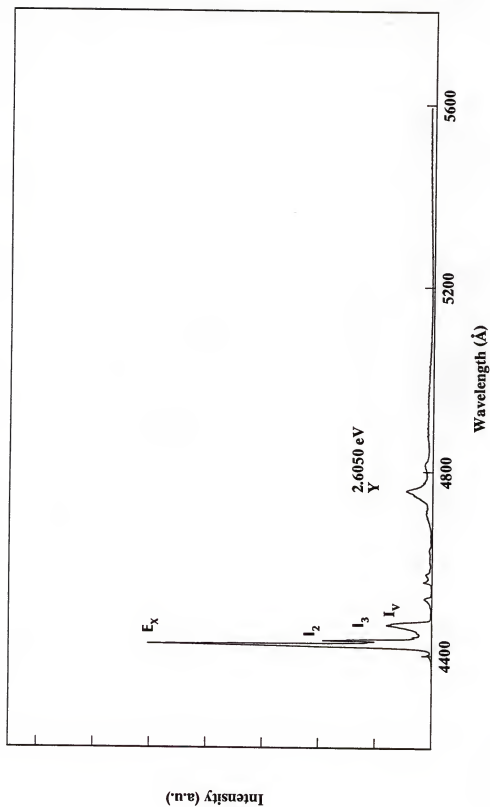


Figure 5.5(a) Low-temperature (24K) PL spectrum recorded from H12 (Low resolution).

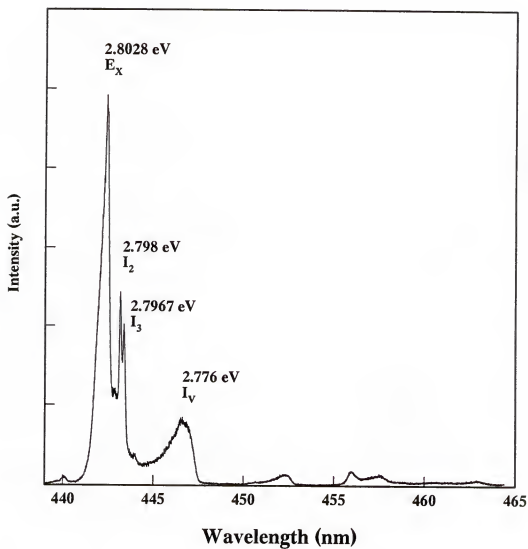


Figure 5.5(b) Low-temperature (24K) PL spectrum recorded from H12.
(High resolution)

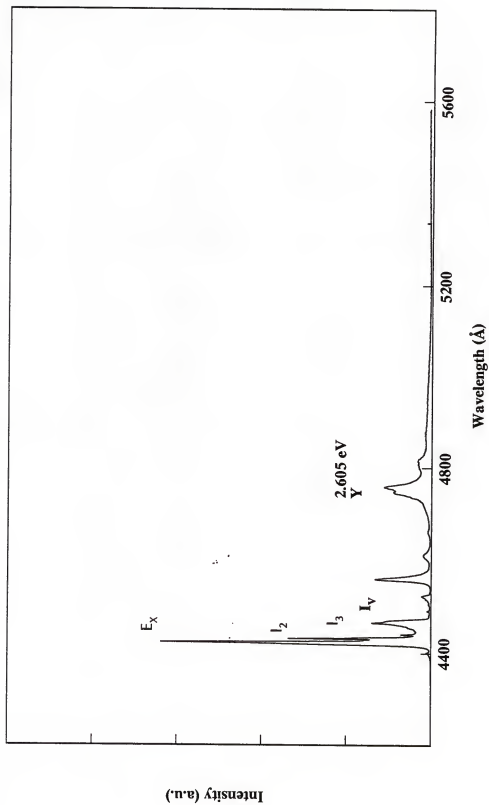


Figure 5.6(a) Low-temperature (24K) PL spectrum recorded from H13 (Low resolution).

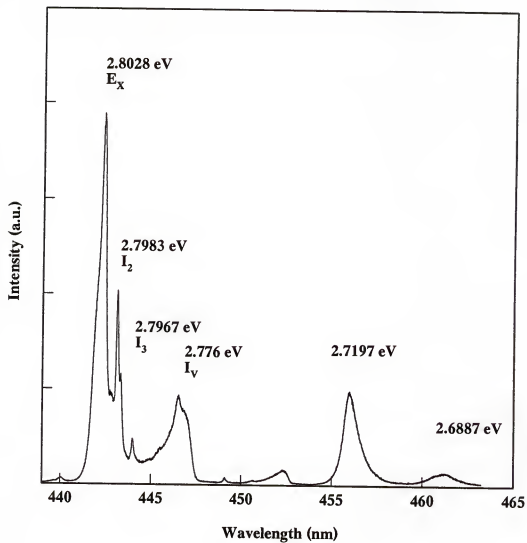


Figure 5.6(b) Low-temperature (23K) PL spectrum recorded from H13. (High resolution).

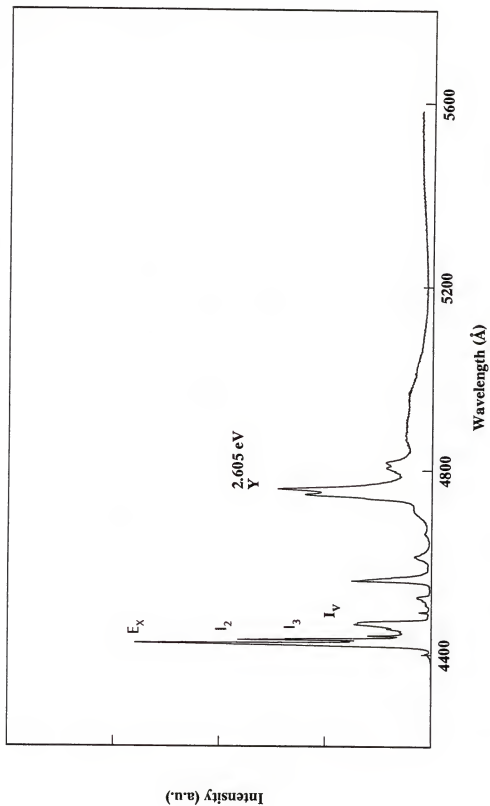


Figure 5.7(a) Low-temperature (23K) PL spectrum recorded from H14 (Low resolution).

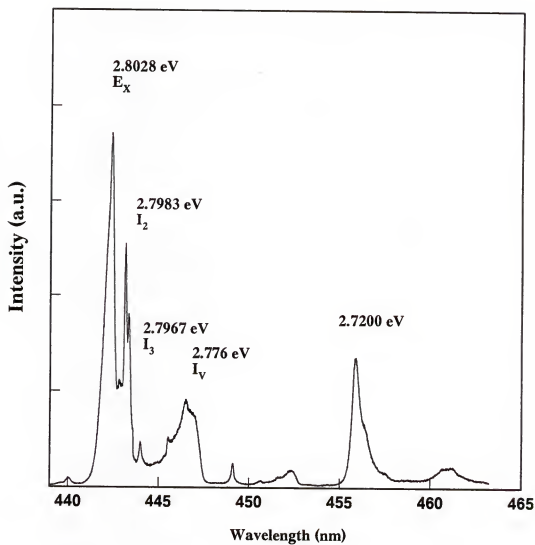


Figure 5.7(b) Low-temperature (23K) PL spectrum recorded from H14.
(High resolution)

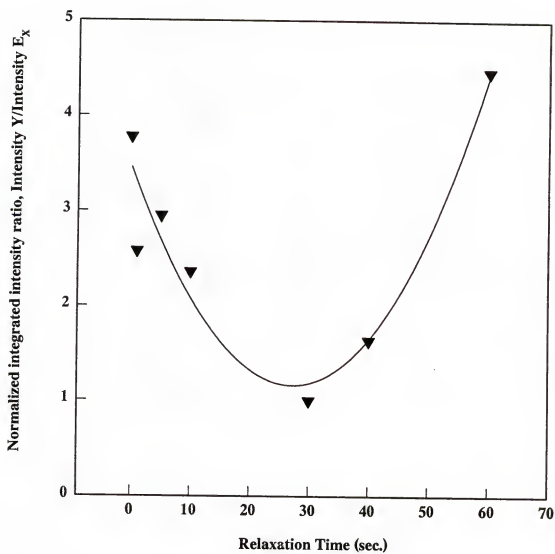


Figure 5.8 Relaxation time dependent low temperature (23K) PL intensity ratio of Y and E_x emissions.

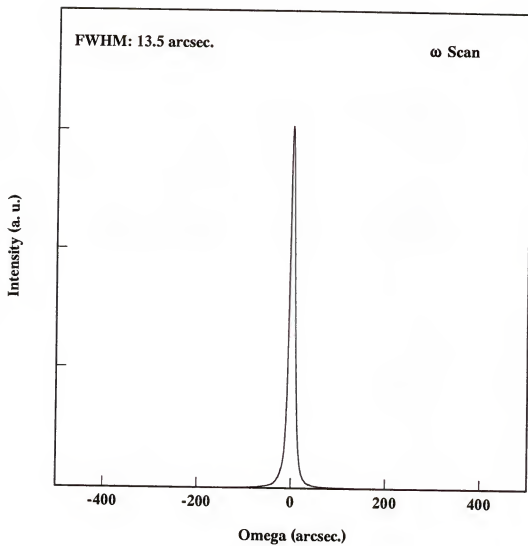


Figure 5.9 X-ray rocking curve of (004) reflection obtained from H8 using analyzer crystal.

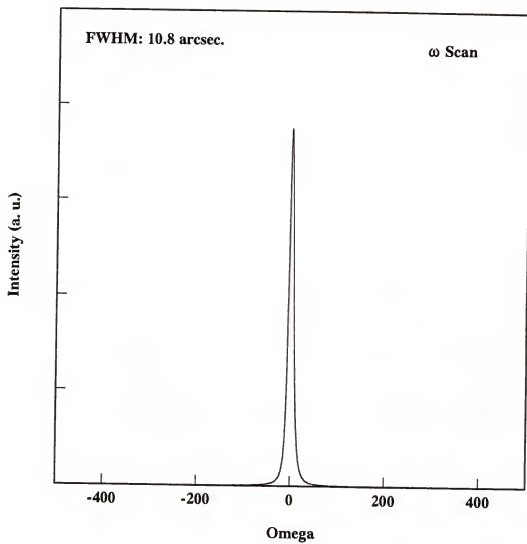


Figure 5.10 X-ray rocking curve of (004) reflection obtained from H12 using analyzer crystal.

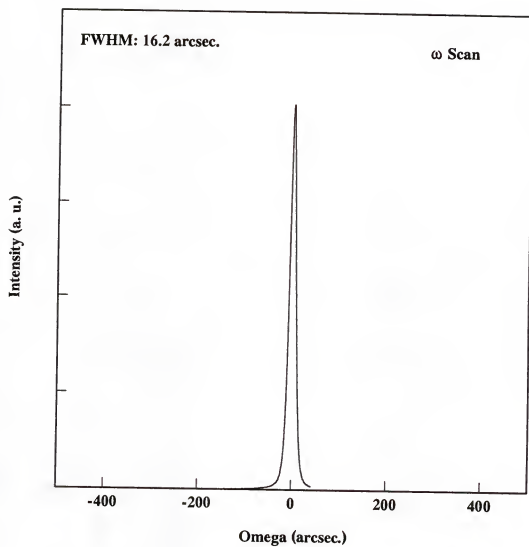


Figure 5.11 X-ray rocking curve of (004) reflection obtained from H14 using analyzer crystal.

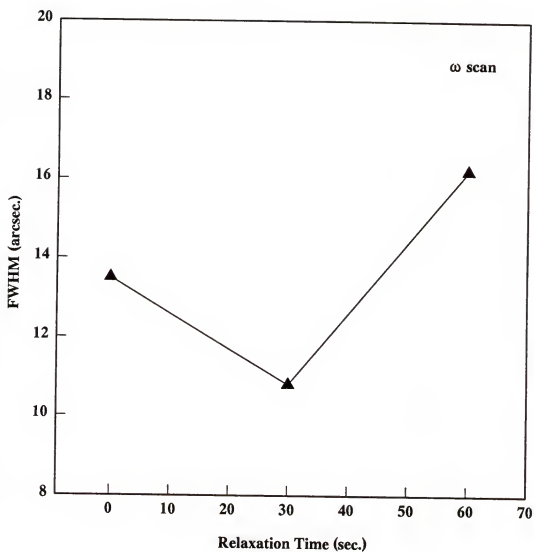


Figure 5.12 Relaxation time dependent FWHM values for the samples H8, H12 and H14. (004) HRXRD was conducted using analyzer crystal.

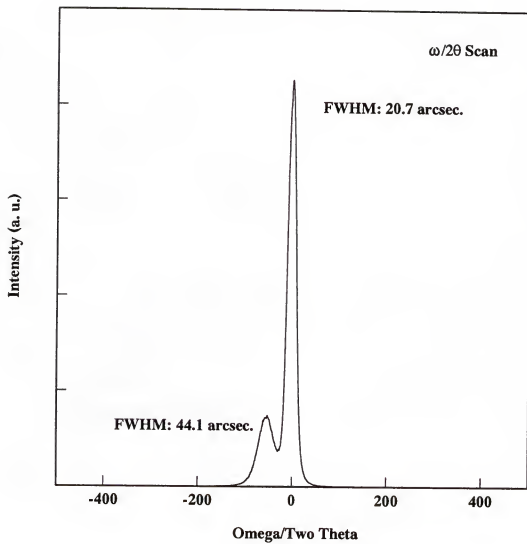


Figure 5.13 X-ray rocking curve of (004) reflection obtained from H8 using analyzer crystal.

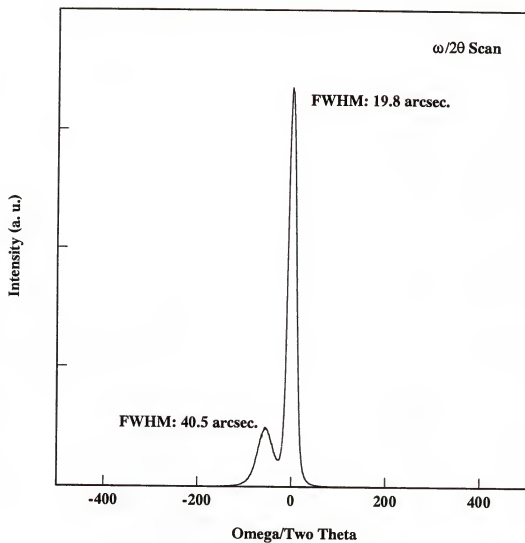


Figure 5.14 X-ray rocking curve of (004) reflection obtained from H12 using analyzer crystal.

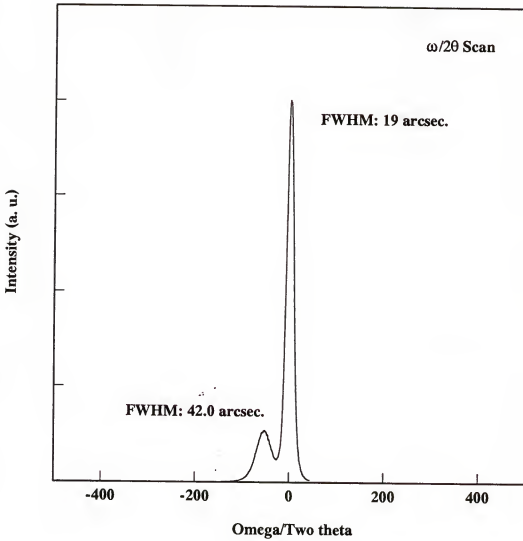


Figure 5.15 X-ray rocking curve of (004) reflection obtained from H14 using analyzer crystal.

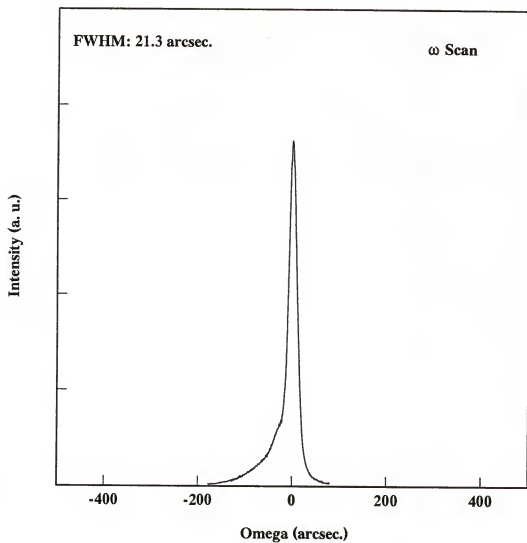


Figure 5.16 X-ray rocking curve of (224) reflection obtained from H8 using analyzer crystal.

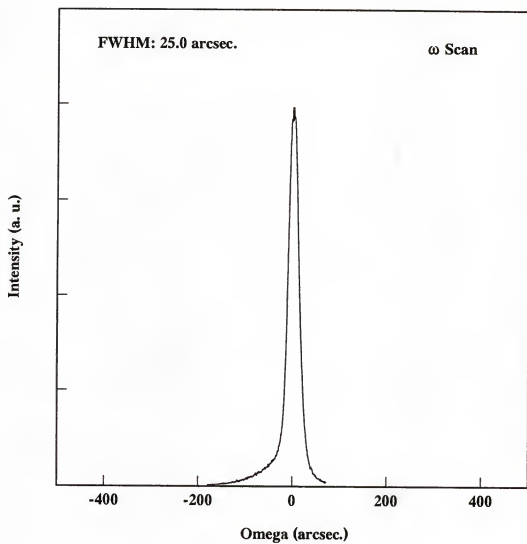


Figure 5.17 X-ray rocking curve of (224) reflection obtained from H12 using analyzer crystal.

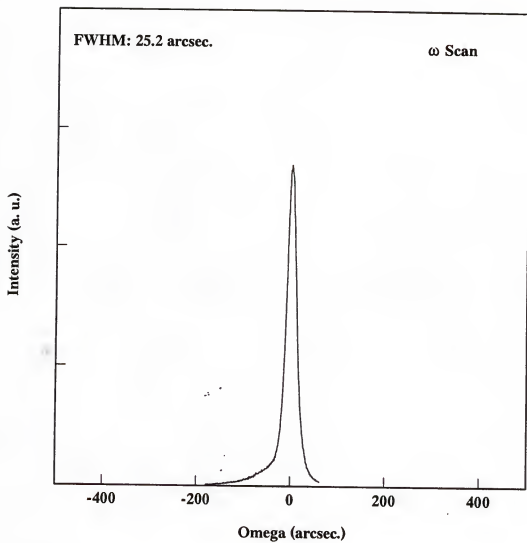


Figure 5.18 X-ray rocking curve of (224) reflection obtained from H14 using analyzer crystal.

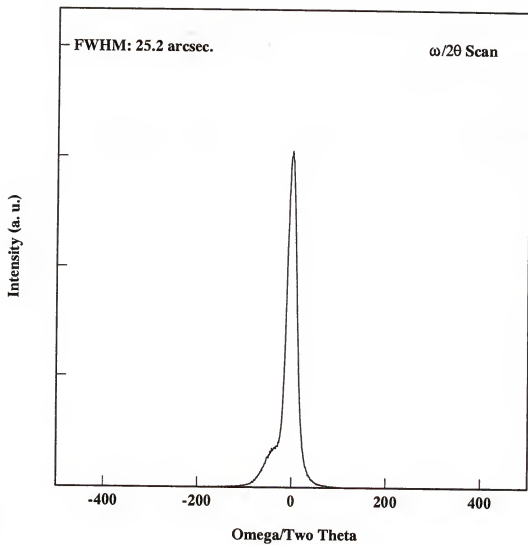


Figure 5.19 X-ray rocking curve of (224) reflection obtained from H8 using analyzer crystal.

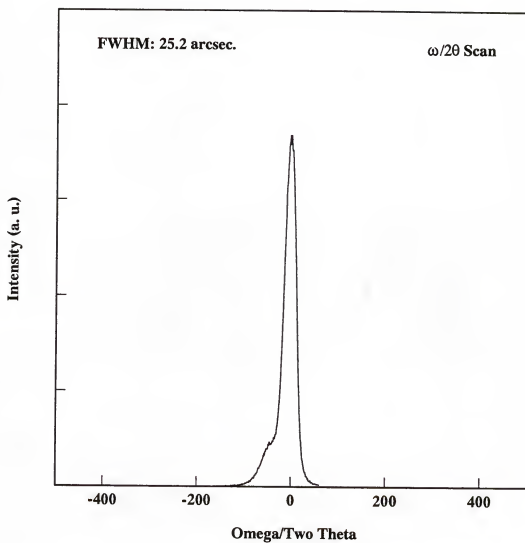


Figure 5.20 X-ray rocking curve of (224) reflection obtained from H12 using analyzer crystal.

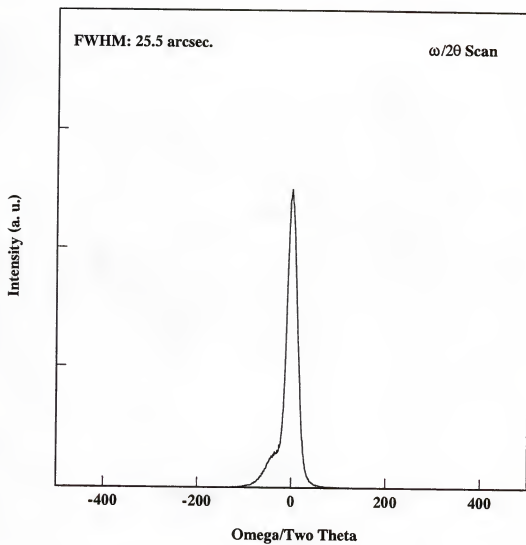


Figure 5.21 X-ray rocking curve of (224) reflection obtained from H14 using analyzer crystal.

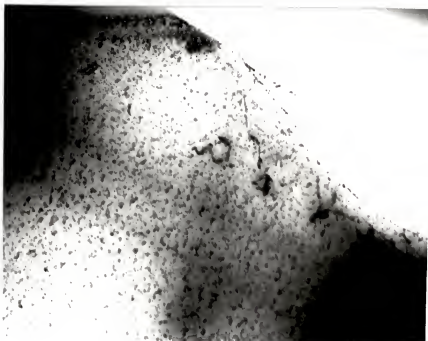


Figure 5.22(a) XTEM micrograph of sample H8. Circular-shaped dislocations are intermittently shown at the homointerface.

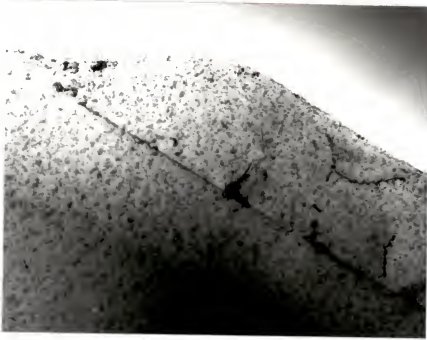


Figure 5.22(b) XTEM micrograph of sample H8 (another location).
Dark line interface is shown in this figure.

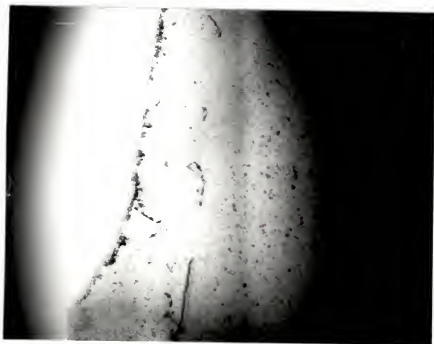


Figure 5.23(a) XTEM micrograph of sample H12. Dark line interface is intermittantly shown at the homointerface.

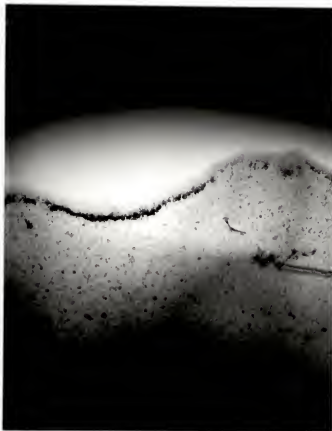


Figure 5.23(b) XTEM micrograph of sample H6 (another location)



Figure 5.24(a) XTEM micrograph of sample H13. Tangled threading dislocations are shown in this figure.

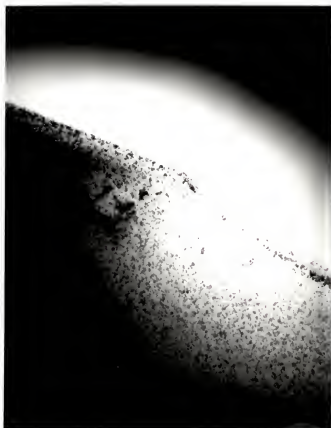


Figure 5.24(b) XTEM micrograph of sample H13 (another location).

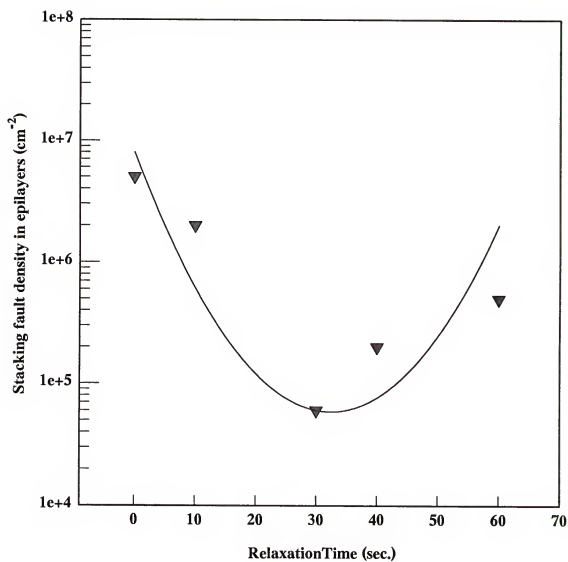


Figure 5.25 Relaxation time dependent stacking fault density determined by EPD test.



Figure 5.26 RHEED patterns recorded from the $[110]$ azimuth (a) during Se exposure, (b) 12 seconds, and (c) 20 seconds after Se shutter closed.

(e)



(d)



Figure 5.26--continued.
RHEED patterns recorded from $[110]$ azimuth (d) 30 seconds and (e) 40 seconds after Se shutter closed.

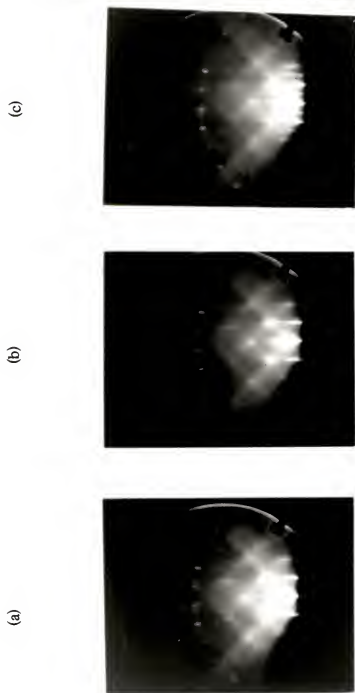


Figure 5.27 RHEED patterns recorded from the [010] azimuth (a) during Se exposure, (b) 28 seconds, and (c) 90 seconds after Se shutter was closed.

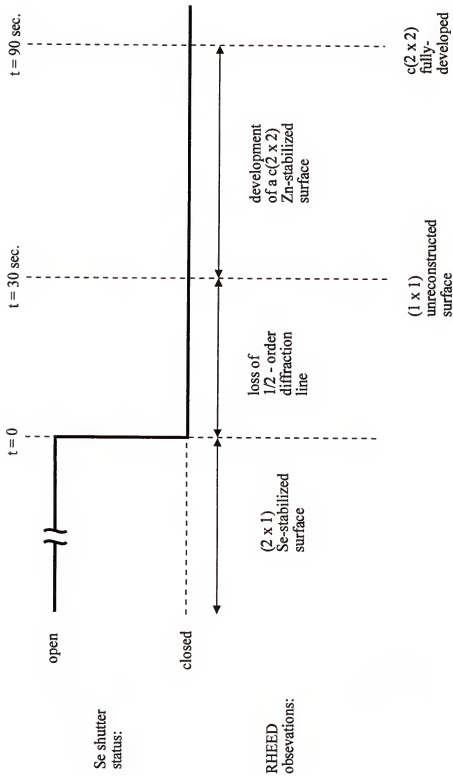


Figure 5.28 Time line for selenium desorption for a substrate temperature of 298 °C.

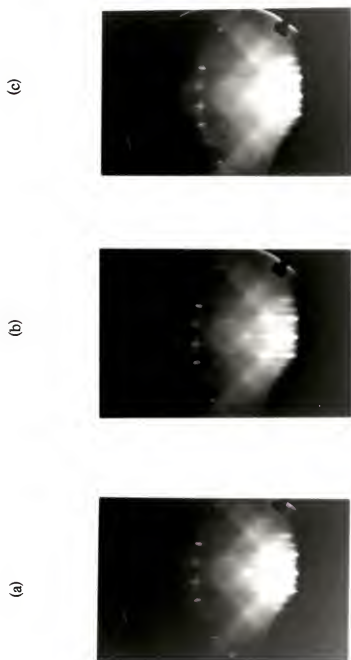


Figure 5.29 RHEED patterns recorded from the [010] azimuth (a) during Zn exposure, (b) 30 seconds, and (c) 5 minutes after Zn shutter was closed.

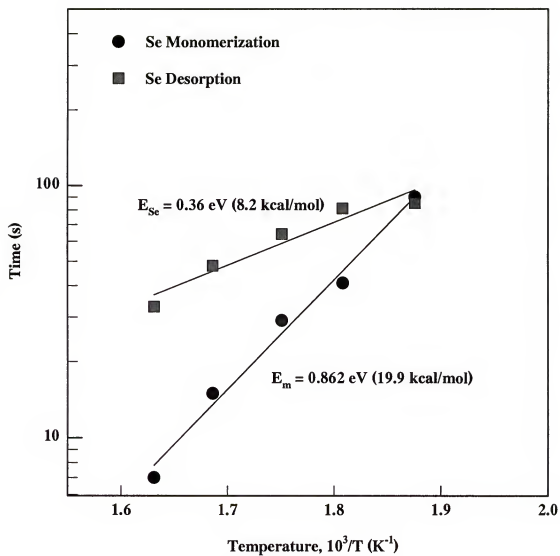


Figure 5.30 Measured values of Se-monomerization time and Se desorption time plotted as functions of reciprocal temperature.

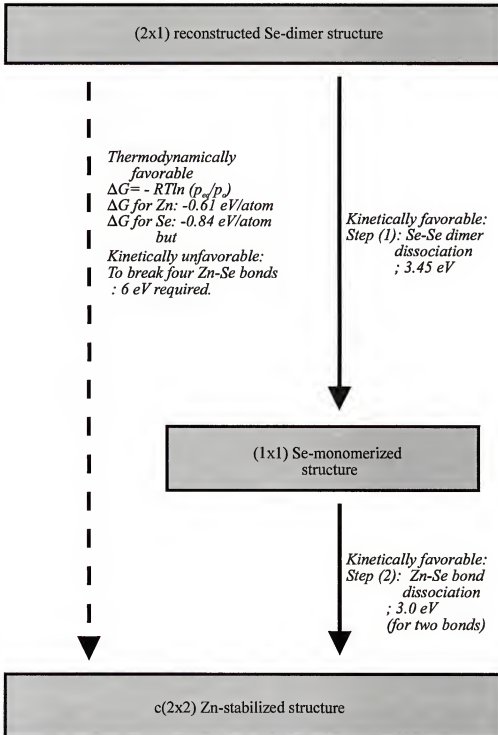


Figure 5.31 Model for Se desorption.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Several conclusions can be drawn from the work described in this dissertation which are as follows.

- 1) A series of four batches of Sumitomo ZnSe wafers was successfully characterized and it was determined that Sumitomo has achieved a significant improvement in wafer quality over time. Specifically, ZnSe wafers in Batch 4 exhibited the narrowest rocking curve linewidths and the smoothest surface morphologies (as smooth as that of the AXT GaAs wafer). However, these wafers still contain impurities and defects (low 10^5 cm^{-2} range) based on low-temperature PL and TEM analyses. Also, hillocks of an unknown source were observed on ZnSe wafer surfaces although the hillock density was greatly reduced in Batch 4 samples. Since the ZnSe wafers in Batch 4 exhibited the highest crystallographic quality, all homoepitaxial growth was performed on ZnSe wafers from Batch 4.
- 2) The ZnSe wafer surface roughness was found to be modified by *ex-situ* UV-ozone treatment and the influence of substrate surface roughness on the quality of MBE-grown ZnSe homoepitaxial layers was examined. It was found, based on HRXRD and PL analyses, that a six minute UV-ozone treatment provided the best homoepitaxial layer quality. It was concluded that even in the best material grown by conventional MBE,

mosaicity and defects (strain) were present as evidenced by extensive 7-crystal x-ray analysis.

3) It was found that a combined thermal/H-atom treatment is superior to conventional thermal treatment for in-situ cleaning of ZnSe wafers in that the H-atom process allowed oxide desorption at a lower temperature (300 °C compared with 500 °C) and resulted in a smoother ZnSe surface as evidenced by the RHEED patterns observed from the cleaned surfaces.

4) The influence of relaxation time on the quality of ZnSe homoepitaxial layers was systematically examined. Sample H12 which was grown using the 30 second relaxation time exhibited the lowest Y/E_x ratio. Since the Y emission is directly related to threading dislocations, the 30 second relaxation time appears to be optimum at least from the PL data. The trend exhibited by PL data (Figure 5.8) with regard to relaxation time variation correlates well with the trend shown by the EPD analysis (Figure 5.25); Sample H12 possesses the lowest stacking fault density of $6 \times 10^4 \text{ cm}^{-2}$. Furthermore, Sample H12 exhibited the narrowest ω rocking curve line width of 10.8 arcsec. (Figure 5.12). Therefore, it is concluded that the optimum relaxation time to deposit high quality homoepitaxial ZnSe layer is 30 seconds.

5) It was found that the Zn-stabilized surface is thermodynamically more stable than the Se-stabilized surface based on Gibbs free energy calculations. Therefore, the system tries to minimize the total Gibbs free energy by desorption of Se atoms leading ultimately to a Zn-stabilized surface in the absence of a Se exposure. It is proposed that the Se desorption process is a two step kinetic process involving step (1), Se-Se dimer bond

breaking with the surface becoming (1x1) unreconstructed, and step (2), breaking of Zn-Se bonds with the surface becoming Zn-terminated.

6) Based on the above considerations, a new growth mode, termed "Surface Relaxation Controlled Epitaxy" (SRCE) was proposed. In this mode, the Zn flux should be exposed just after the (2x1) Se-stabilized surface is fully relaxed to the (1x1) unreconstructed surface. It can be concluded that it is possible to significantly minimize the defect density (both stacking faults and threading dislocations) in ZnSe films by employing the SRCE growth mode.

It is recommended that the new growth mode be applied to wide-gap II-VI/GaAs heteroepitaxial layers. In principle, when the appropriate conditions are found, stacking fault densities in these materials could be dramatically reduced.

APPENDIX

ATOMIC FORCE MICROSCOPY

Atomic force microscopy (AFM) was used to examine surface roughness. Since AFM is a relatively new technique, the basic principle of operation and characteristics are outlined in this section.

Basic principle

A schematic of a generalized atomic force microscope is illustrated in Figure A1. AFM images are obtained by measuring the interaction forces between a cantilever-mounted sharp tip and the surface of a sample mounted on an x, y, z piezo scanner as the tip is scanned over the sample surface (actually, the sample is scanned under the tip). This force, a function of the distance between the tip and the sample surface, can be kept at a constant level by a feedback mechanism. Most AFMs currently on the market detect the position of the cantilever using optical techniques. A laser beam reflects off the back of the cantilever onto a position-sensitive photodetector (PSPD) as shown in Figure A2. As the cantilever bends due to the tip interaction with the sample surface, the position of the reflected laser beam on the detector shifts. The PSPD itself can measure displacement of light as small as 10 Å. The ratio of the path length between the cantilever and detector to the length of the cantilever itself produces a mechanical amplification. As a result, the system can detect sub-angstrom vertical movement of the cantilever tip. Indeed, the AFM system used for these experiments (NanoScope III SPM)

has a vertical resolution of $0.1 \text{ \AA}$. Finally, the measured cantilever deflections allow a computer to generate a map of the surface topography. AFM can be used to investigate insulators and semiconductors as well as conducting materials.

Imaging modes

The AFM can be operated in different modes appropriate to the application. There are three different operating modes available, namely, contact mode, non-contact mode, and tapping mode, each dependant upon the net forces between the probe and sample.

Contact mode. In contact mode, also known as "repulsive mode," the AFM is operated in the repulsive region in the force-distance curve (Figure A3). In this mode, the cantilever is curved away from the sample due to repulsive forces and the AFM tip makes soft physical contact with the sample surface. The cantilever to which the tip is attached has a low spring constant, lower than the effective spring constant holding the atoms of the sample together. As the scanner gently traces the tip across the sample (or, the sample under the tip), the contact force causes the cantilever to bend to accommodate changes in the surface topography. As shown in Figure A3, the slope of the van der Waals curve is very steep in the repulsive or contact region. As a result, the repulsive van der Waals force will balance almost any force that attempts to push the atoms of the tip closer to the atoms on the sample surface. In AFM, then, as the cantilever pushes the tip against the sample, the cantilever will bend rather than forcing the tip atoms closer to the sample atoms. When the AFM is used in the ambient atmosphere, one should be careful about the capillary forces due to a thin water layer often present on the sample surface.

Non-contact mode. When the AFM is operating in the attractive region of the force-separation curve (see Figure A3), it is in the “non-contact” or “attractive mode”. In this mode, the AFM cantilever is curved toward the sample. The tip-to-sample distance is generally in the range of 50 to 100 Å. In the non-contact AFM region in Figure A3, the slope of the van der Waals curve is shallower than in the contact region. This shallow slope results in smaller cantilever deflections in response to changes in tip-to-sample separation. Furthermore, a cantilever stiffer than that used in contact mode must be used because more flexible cantilever would flop onto the sample surface as soon as its tip came close enough to the sample surface to experience the attractive force. In non-contact mode, the resonant frequency of the cantilever is kept constant by means of a feedback system that moves the scanner on which the sample is mounted up and down. By keeping the resonant frequency constant, the system also keeps the average tip-to-sample distance constant and the motion of the scanner is used to generate the data set. Non-contact mode involves very low total force between tip and sample, generally about 10^{-12} N. This low force is advantageous for investigation soft materials. In addition, contamination of the sample surface can be prevented.

Tapping mode. Tapping mode is a variation of the contact mode, but is operationally similar to non-contact mode. In tapping mode, the cantilever oscillates at its resonant frequency with a high amplitude, on the order of 1000 Å. The tip touches the sample during each oscillation (hence the term “tapping mode”). Tapping mode is less likely to damage the sample than contact mode because it eliminates lateral forces

(friction or drag) between the sample and the tip. Therefore, in this study, tapping mode was employed in order to protect the ZnSe wafer surfaces.

Roughness measurements

In this study, the surface roughness of the ZnSe wafers was evaluated using a NanoScope III AFM obtained from Digital Instruments Inc. Operating in air, the root mean square (RMS) of height variation was recorded. RMS (R_q) is defined as the standard deviation of the Z (height) values within the given area.

$$R_q = \sqrt{\frac{\sum (Z_i - Z_{ave})^2}{N}}$$

where Z_{ave} is the average of the Z values within the given area, Z_i is the current Z value (height), and N is the number of points within the given area.

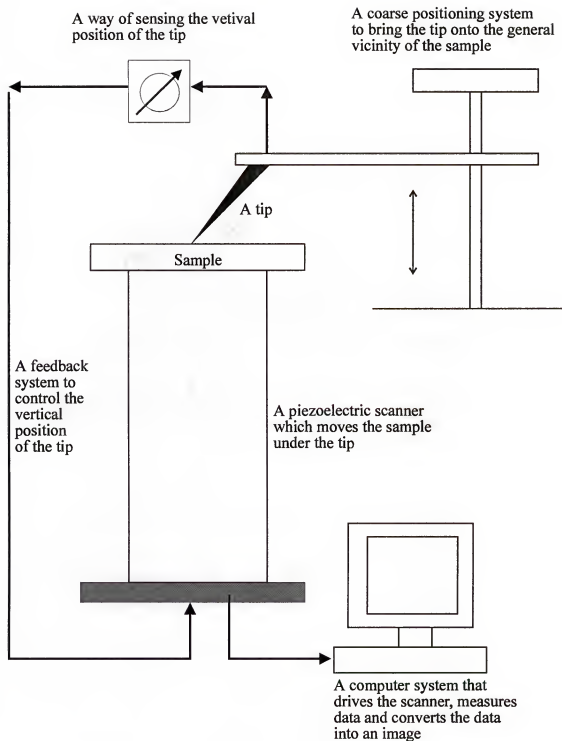


Figure A1 A schematic of a generalized atomic force microscope.

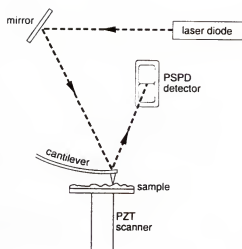


Figure A2 Schematic of optical-deflection technique for detecting cantilever deflection. (After Nanoscope III manual)

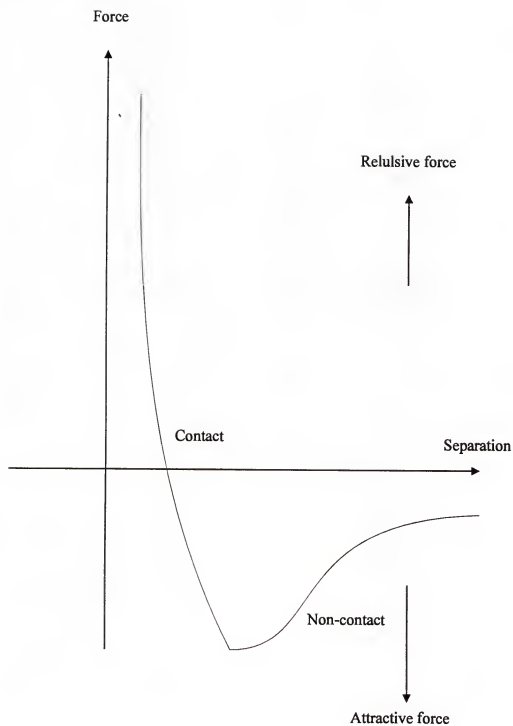


Figure A3 Van der waals force versus tip-to-sample separation.

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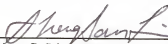
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